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THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE BALTIMORE MEETING.

THE Baltimore meeting of the society held December 27 and 28, 1893, was in every respect most successful. This is due in large part to the local committee of arrangements, which in turn expresses itself as under great obligations to Prof. Ira Remsen.

The sessions were held Wednesday, December 27 and 28, 1893, in Prof. Remsen's lecture room in Hopkins Hall, Johns Hopkins University.

Addresses of welcome were made by D. C. Gilman president of the university, and Ira Remsen Prof. of chemistry.

President Gilman, in behalf of the Johns Hopkins University, extended a hearty welcome to the society and offered it all the facilities for its work which the libraries, halls, and laboratories of the university would afford. He referred to a medieval custom, the migration of students from one seat of learning to another, and compared it with the modern and American usage, which transports professors, instead of students, from one point to another. Thus the Christmas and Easter holidays, as well as the long vacation of summer, are now the favorite times for the assembling of literary and scientific associations like that now welcomed to Baltimore.

He then briefly described the buildings of the university, and made an allusion to the many distinguished men of science, from Europe as well as from this country, whose voices have been heard within the walls of Hopkins Hall where this American Chemical Society now holds its annual meeting.

Prof. Remsen in welcoming the society to the chemical lab-

oratory gave a brief account of the way the present building gradually came into being. The laboratory is called Dalton Hall, a name that has a deeper significance than appears at first sight. Dalton was a member of the Society of Friends, and the founder of the Johns Hopkins University and several of those whom he selected to act as trustees of the university were also members of this society. Certainly to every thinking chemist the name of Dalton is a most inspiring one. He gave us some of the greatest thoughts of our science, and laid the foundations of the most profitable speculations in regard to the constitution of matter. His work has been of inestimable value, and has contributed very largely to the advancement of the science of chemistry. The speaker then said that in emphasizing the science of chemistry, as he is very apt to do, he did not wish to be misunderstood. Everyone recognizes the importance of the chemical industries. These need no spokesman. The fact that pure science is not, a mere luxury, but of importance to mankind, is, however, often lost sight of, and it seems desirable that occasionally a voice should be raised in its defence. While this was not necessary on the present occasion, the speaker wished to declare his own attitude, in order, as far as possible, to avoid misunderstanding. Science and industry must go hand in hand. They are mutually dependent. The man of science who speaks with disrespect of the industries is certainly short sighted; and the same is true of the industrial chemist who speaks disrespectfully of science.

In replying to the addresses of welcome the president, Harvey W. Wiley, said that the present membership of the society was 681, of whom 542 had paid all dues. The names added during the year numbered nearly 400. He referred to the valuable work accomplished by the older members and the sacrifices they had made in order that the society might become truly, as well as in name, a national organization. These remarks applied especially to the members of what is now the New York Local Section.

There are now over 4000 professional chemists in the United States, and this allows ample opportunity for enlargement of the membership which is rapidly going on.

We rejoice that there is no longer reason that Americans should go abroad to study chemistry. Facilities equal to those offered abroad are now to be had at the Johns Hopkins University and at other institutions in our own land.

The president then read the annual address which has already been printed in the January issue of this JOURNAL.

G. F. Barker read a memorial of the late Dr. F. Sterry Hunt, at the conclusion of which the members rose to honor his memory.

After a recess of five minutes, Edward Hart was elected secretary pro tempore. The reports of the secretary, treasurer, librarian and editor were then read and adopted.

The treasurer's report follows:

TREASURER'S REPORT.

RECEIPTS.

Balance on hand, January 1st, 1893	$ 518.41
Cash received from dues for 1893	1,994.79
" " " " " 1894	200.00
" " " " " 1895	5.00
" " " arrears of dues	105.15
" " " subscriptions to JOURNAL	72.00
" " " advertisements in JOURNAL	213.45
" " " sales of back numbers	67.47
" " " Initiation fee (F. J. Wulling)	5.00
" " " exchange	.07
	3,181.34

EXPENDITURES.

General expenses	$ 380.42
Journal of 1892	654.73
" " 1893	1,784.70
New York Local Section	115.00
Cincinnati Local Section	59.93
Providence " "	18.33
Baltimore meeting	84.18
Overpayment of Dues returned	5.00
Initiation fee returned (F. J. Wulling)	5.00
Balance on hand in bank of the Metropolis	74.05
Checks on hand	—
	3,181.34

CHAS. F. MCKENNA, Treasurer.

No bills or claims, presented up to date and audited, remain unpaid. Accounts examined and found correct, E. and O. E.

FRANK T. KING,
A. P. HALLOCK,
DURAND WOODMAN. } Finance Committee.

New York, December 22, 1893.

Reports from the secretaries of the New York, Rhode Island, and Washington Sections were read, reporting a good attendance and the presentation of numerous papers at the meetings.

The New York Section has allied itself with other scientific bodies in New York City forming collectively the Scientific Alliance. There is no amalgamation in this nor does the council of the alliance to which each society delegates three members have any control over the internal affairs of the constituent societies. The present membership is 147 a gain of fifteen during the year. Total expenses for the year ending October 6, $88.60. Present officers, Peter T. Austen, chairman; M. Loeb, secretary and treasurer; A. A. Breneman, Wm. McMurtrie, and A. C. Hale, executive committee; P. T. Austen, Wm. McMurtrie, and J. H. Stebbins, delegates to the Scientific Alliance.

The Rhode Island Section reports an addition of one name to its membership making a total of seventeen members. Nine meetings were held from September 1, 1892, to July 1, 1893, at which numerous papers of interest were presented. The officers are, John Howard Appleton, Chairman; E. E. Calder, secretary-treasurer; and the chairman and secretary-treasurer, *ex-officio*, and Charles Catlin, executive committee.

The Washington Section. At the meeting of the Washington Chemical Society held May 11, 1893, the society voted to become a section of the American Chemical Society, and certain amendments to the constitution were presented to make it conform to such action. These amendments and a revised constitution were adopted December 14, which consummates the formation of the Local Section. No meetings were held between May 11, and October 31. The section has 94 members. The officers are F. P. Dewey, president; Cabell Whitehead and K. P. McElroy, vice-presidents; E. A. de Schweinitz, treasurer; A. C. Peale, secretary; F. P. Dewey, T. M. Chatard, K. P. McElroy, E. A.

de Schweinitz, A. C. Peale, H. W. Wiley, F. W. Clarke, Cabell Whitehead, and R. B. Warder, executive committee.

The Cincinnati Section presented no report. Since the meeting a report from the local secretary has been received which shows that the present membership is fifty-five a gain of seven. Eight meetings have been held at which numerous papers were read. The officers are: president, C. R. Stuntz; vice-presidents, W. Mumper and E. Twitchell; secretary, W. Simonson; treasurer, H. E. Newman; and directors, W. Dickore, J. U. Lloyd, A. C. Ramsay and E. C. Wallace.

The following papers were then read:

The Widespread Occurrence of Barium and Strontium in Silicate Rocks. *W. F. Hillebrand.*

The Estimation of Small Amounts of Barium and Strontium in Silicate Analysis. *W. F. Hillebrand.*

A Plea for Greater Completeness in Chemical Rock Analysis. *W. F. Hillebrand.*

A Study of the Distribution of the Oleo-resins in Pinus Palustris. *Oma Carr.*

Salicylic Acid in Food. *K. P. McElroy.* Read by title.

Utilization of Garbage. *Bruno Terne.* Read by title.

Adjourned at 2 P.M.

In the afternoon a visit was paid to the works of the Baltimore Copper Smelting and Rolling Company, under the guidance of members of the local committee. The raw material consists of Anaconda Matte which is worked up into copper by the ordinary method of roasting and smelting. The impure copper is then subjected to electrolysis and subsequently melted and cast. Another portion of the roasted copper oxide is boiled with sulphuric acid and the blue vitriol crystallized out and sold. Silver is separated by the addition of a small amount of common salt.

In the evening a dinner complimentary to the visitors was given by the local committee at the Eutaw House. Dr. Wm. Simon acted as toastmaster and H. W. Wiley, Wm. McMurtrie, Ira Remsen, F. W. Clarke, J. H. Appleton, Edward Hart, W. L. Dudley, and C. B. Dudley responded to toasts.

THURSDAY, DECEMBER 28.

Papers were read as follows:

Some Facts Relating to Type Writing Machine Oils. *Thomas Taylor.*

Report on the Determinations of Atomic Weights published during 1893. *F. W. Clarke.*

The Detection of Strychnine in an Exhumed Human Body. *W. A. Noyes.* Read by Edward Hart.

The Importance of the Study of Biochemistry. *E. A. de Schweinitz.* Read by C. E. Munroe.

Upon Uniformity in Sampling and Assaying Copper Bullion. *G. W. Lehmann.* Read by title.

The Preservation and Arrangement of Chemical Abstracts and Clippings. *Thomas M. Chatard.*

Historical Notes on the Electro-metallurgy of Zinc. *Charles Platt.*

The Phenylhydrazin Test for Glucose in Urine. *C. E. Pellew.* Read by title.

Expert Testimony. *W. P. Mason.*

The Boric Acid Springs of Tuscany. *W. P. Mason.*

Phosphorus in Steel. *C. B. Dudley.*

Some Points in the Volumetric Estimation of Phosphorus. *C. B. Dudley.*

Determination of Phosphorus by the Molybdate Method in Presence of Arsenic in Iron, Steel and Ores. *James O. Handy.* Read by C. B. Dudley.

The Analysis of Malt. *J. A. Miller.* Read by title.

Determination of Nickel in Steel. *Jos. Westesson.* Read by title.

Preliminary Note on Electrical Organic Analysis. *Edward Hart.*

Convenient Resistance Board for Use with Blackened Lamps. *Edward Hart.* Read by title.

After a recess of five minutes the secretary read a telegram of congratulation from A. B. Prescott, of Ann Arbor, Mich., as follows:

ANN ARBOR, MICH., December 26, 1893.

Prof. H. W. Wiley, or Secretary American Chemical Society,
Baltimore, Md., (Hotel Rennert).

"I rejoice with Society upon the results of ninety-three; the membership enrolled, the JOURNAL established, the organization effected and the congress of chemists overflowing, each an event in American Chemistry; an event international is Bolton's Bibliography of Four-Hundred Years. With regret that I must be absent,"

ALBERT B. PRESCOTT.

The secretary was instructed to make a suitable response.

The report of the committee of canvassers was presented showing the election of H. W. Wiley as president; A. C. Hale, secretary; C. F. McKenna, treasurer; F. E. Dodge, librarian; C. F. Chandler, P. T. Austen, C. A. Doremus and H. C. Bol-

ton as directors to serve two years. C. B. Dudley, C. E. Munroe, Wm. McMurtrie and J. H. Appleton to serve as councilors for three years.

H. W. Wiley, chairman of the committee on new charter, reported that he had been unable to obtain a meeting of the committee, but that on his individual responsibility he reported in favor of the surrender of the New York Charter and the organization of the society under a new charter to be obtained from Congress. At the suggestion of Dr. McMurtrie and C. E. Munroe the matter was referred to the council for further examination with power to act.

On motion of Edward Hart the president was authorized to appoint a committee of seven to include the members of the committee on papers and publications to act as an advisory board on matters pertaining to the "style" to be used in the JOURNAL. (nomenclature, spelling, punctuation, etc.). The president subsequently named the following persons to act as members of this committee: Edward Hart, chairman; J. H. Long, Edgar F. Smith, A. B. Prescott, G. C. Caldwell, T. H. Norton and H. Carrington Bolton.

On motion of J. H. Appleton a committee of seven was appointed to petition Congress for a more specific wording of that part of the tariff bill pertaining to importation of duty free apparatus and supplies for scientific work. The committee consists of C. E. Munroe, chairman; H. B. Nason, Edward Hart, E. F. Smith, J. H. Appleton, A. B. Prescott, and W. L. Dudley.

Dr. Wiley thanked the society for the honor done him in a re-election to the office of president. He believed, however, as the office of president was entirely honorary that two terms for one person was a mistake. As a mistake had now been made he felt bound to accept, especially as a declination to serve would put the council to inconvenience and delay business that should be attended to promptly.

Mr. C. F. McKenna offered his resignation as treasurer, stating that he found the work required so much time that he felt unable to longer attend to it. Referred to the council.

On motion of F. W. Clarke the thanks of the society were voted to the local committee of arrangements, to President D. C.

Gilman and Prof. Ira Remsen, of Johns Hopkins University, for courtesies extended, to the Baltimore Copper Smelting and Rolling Co., the Lazaretto Chemical and Fertilizer Co., and the Maryland Steel Co., for the privilege of inspecting their plants, and to Baker, Whitely and Co., and the Rasin Fertilizer Co. for transportation.

Adjourned.

In the afternoon the members visited the works of the Maryland Steel Co., at Steelton. The tugs Sea-Wall and Chicago carrying the party down the bay.

These works comprise four large blast furnaces, two twenty ton Bessemer converters and a complete ship building plant. A recent addition is the immense shears operated by hydraulic power which were used in lifting Krupp's gun from the vessel to the car upon which it was transported to Chicago. The party were taken through the works by Mr. Frank T. King and through the Bessemer Steel department by Mr. G. F. Knapp.

Local Committee of Arrangements.—C. P. Van Gundy, chairman; W. B. D. Penniman, secretary; Wm. Simon, W. J. Gascoyne, R. D. Coale, Chas. Glaser, G. W. Lehmann, A. R. L. Dohme, A. J. Corning, Wm. Glenn and G. A. Liebig, Jr.

REGISTER OF MEMBERS IN ATTENDANCE.

Wm. McMurtrie,
Chas. F. McKenna,
P. Fireman,
Walter B. Randall,
Charles L. Parsons,
Chas. B. Dudley,
E. W. Allen,
W. D. Bigelow,
H. W. Wiley,
Edward Hart,
W. J. Gascoyne,
W. B. D. Penniman,
A. L. Browne,
W. Liman,
C. P. Van Gundy,
Wm. Bromwell,
Wm. Simon,
A. R. L. Dohme,
R. D. Coale,
W. F. Hillebrand,
G. L. Spencer,
H. B. Nason,
Wm. P. Mason,
J. H. Appleton,
E. C. Franklin,
Thomas Taylor,
G. A. Chalmot,
W. R. Orndorff,
A. P. Sharp,
Charles Platt,
R. M. Parks,
Sam'l P. Sadtler,
Thomas M. Chatard,
H. H. Hawling,
G. B. Pfeiffer,
G. F. Barker,
Geo. Steiger,
Robt. B. Warder,

Chas. Glaser,
Wm. Glenn,
A. J. Corning,
Charles E. Munroe,
Eugene Byrnes,
Wirt Tassin,
August E. Knorr,
Oma Carr,
T. C. Trescott,
Wm. H. Krug,
F. W. Clarke,
W. P. Cutter,
T. R. Wolf,
H. B. Hodges,
Edgar F. Smith,
Wm. M. Groevsnor, Jr.,
W. L. Dudley,
G. W. Lehmann,
J. B. Littlewood,
W. N. Mumper,
John Johns,
Edgar Richards,
Marcus Benjamin,
Lyman B. Hall.

THE WIDE-SPREAD OCCURRENCE OF BARIUM AND STRONTIUM IN SILICATE ROCKS.[1]

By W. F. Hillebrand.

AMONG the mass of published analyses of igneous eruptive and metamorphosed eruptive rocks, those in which barium and strontium are noticed are few indeed, unless the work has been of a special nature, like that of Sandberger in the development of the lateral secretion theory. Yet the very numerous analyses of igneous eruptive rocks of all ages and kinds made in the laboratory of the United States Geological Survey during the past thirteen years, have shown that these elements are distributed widely and in considerable quantity, in the United States at least, and doubtless elsewhere.

The percentages of barium and strontium oxides when present are usually below 0.1 per cent. each, but higher amounts are by no means uncommon, and for certain districts seem to be the rule rather than the exception. Within the past year two series of rocks from Colorado and Montana have been analyzed, both of which are noteworthy for the high percentages of barium found in them. Of seven rocks constituting the Colorado series six held from 0.13 to 0.18 per cent. BaO, while in the seventh the percentage was 0.43. The SrO ranged from 0.07 to 0.13 per cent. for six, and was 0.28 per cent. for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acid and intermediate types, the range of BaO

[1] Read at the Baltimore meeting, December 27, 1893.

was from 0.19 to 0.37, with an average holding of 0.30 per cent. Three others of the same series contained 0.10 per cent. or less, while the seventeenth carried 0.76 per cent. BaO. The SrO ranged from 0.37 per cent. in the last instance to an average of 0.06 per cent. for the other sixteen.

In view of the above showing the question arises, why was not this general distribution sooner recognized? The answer is undoubtedly given by the statement that it has not been the custom among chemists to look for barium and strontium in analyses of the kind under discussion, and doubtless for the following reasons:

1st. A belief on the part of many that the two elements were absent from most rocks, this belief being based on the supposed rarity of the few rock-constituting minerals known to contain barium and strontium as noteworthy constituents.

2nd. Admitting the possibility of their presence in minute quantities, the unimportance as an aid to classification by the lithologist of the knowledge that a rock may contain a few hundredths of one per cent., more or less, of barium or strontium.

The unsoundness of the first argument has been sufficiently demonstrated by the data given above for rocks of the United States, which show likewise what serious errors may be incurred by neglect to test for the elements in question. Barium and strontium carrying minerals, sometimes with high percentages of one or both, are more common rock constituents than was formerly supposed.

With regard to the second point it may be said that if the present decade or the next may be unable to make use of the knowledge referred to, this will probably not hold true of the lithologists of a still later period—an argument perhaps equally applicable to other elements than barium and strontium.

Regarding a further reason why barium has undoubtedly often been overlooked, the reader is referred to the following paper.

THE ESTIMATION OF SMALL AMOUNTS OF BARIUM AND STRONTIUM IN SILICATE ANALYSIS.[1]

By W. F. Hillebrand.

In testing qualitatively for barium and strontium in the course of analysis of natural silicates it has probably been the custom to rely upon the spectroscopic examination of the ignited calcium oxalate, on the assumption that, notwithstanding the well-known greater solubility of barium and strontium oxalates over the corresponding calcium salt, the latter would carry down enough of the former to render detection of barium and strontium by aid of the spectroscope a matter of no difficulty.

This assumption in the case of strontium is well founded as I have observed times without number, but it may be entirely fallacious in the case of barium. The twice precipitated calcium oxalate of the analyses marked "later" in the next following paper, affording a very strong spectroscopic reaction for strontium, but failed to give one for barium, although the oxide of this element was a constituent of the rocks up to 0.76 per cent., and simply because the latter had been entirely kept in solution by the large amounts of ammonium chloride present. This observation suggested at once an explanation for the apparent rarity of barium in the silicate rocks of the earth's crust, and opened up a field for investigation as to the best course to pursue in the separation and estimation of the three alkaline earth metals under the conditions generally prevailing in rock analysis, that is to say, great excess of calcium over barium and strontium in presence of magnesium and large amounts of sodium and ammonium chlorides.

Brief consideration sufficed to reject recourse to collective precipitation of the alkaline earths by ammonium carbonate because of the well-known incompleteness of such precipitation under the prescribed conditions.

It seemed better to seek a separation of barium at the outset. This conclusion was fortified by the results of experiments undertaken to ascertain the behavior of strontium under conditions similar to and differing from the above. A large number of experiments were made with calcium, strontium, and barium sepa-

[1] Read at the Baltimore Meeting, December 27, 1893.

rately, and then with mixtures of the former and either strontium or barium. The absolute amounts experimented with were kept low in order that the conditions usually obtaining in rock analysis might be as nearly as possible preserved. It was not for a moment expected that an exact method of separating considerable amounts of barium from either calcium or strontium would be discovered. The most that was hoped for was to work out a method suitable of application where relatively small amounts of strontium and barium occur with relatively large amounts of calcium. The outcome only in a measure fulfilled the hope raised by a few preliminary tests, but the results seem to be of sufficient interest to merit somewhat detailed description.

The precipitates were formed in ammoniacal solution at a boiling heat and were allowed to stand over night before filtering. They were washed but once or twice with cold water because of the very marked solubility of both strontium and barium oxalate in hot water, and even in cold water if the washing is prolonged. The filtrates were evaporated to dryness, ammoniacal salts were removed by heat, and after solution of the residue strontium and barium were precipitated as sulphates, the former after addition of alcohol. The sulphates were, when necessary, tested spectroscopically. The amounts of the different salts taken are purely arbitrary, except that the highest weights for BaO are the chemical equivalents of the highest for SrO.

FIRST SERIES.

	Amount taken calculated as oxide.		$(NH_4)_2C_2O_4.H_2O$, amount in excess of that required for conversion of total bases to oxalates.	NH_4Cl	Total bulk of solution.	SrO in filtrate.	
	SrO	CaO	Grams.	Grams.	Cubic centimeters.	Weight.	Per cent.
1	0.0343		½	10	250	0.0080	23.3
2	0.0343		1	10	250	0.0045	13.1
3	0.0343		2	10	250	0.0032	9.3
4	0.0343	0.0560	1	10	250	0.0036	10.5
5	0.0343	0.0560	1½	10	250	0.00275	8.0
6	0.0343	0.0560	2½	10	250	0.0023	6.7
7	0.00384	0.0560	1	5	250	0.0003	7.8
8	0.00384	0.0560	1	10	250	0.0005	13.0
9	0.0010	0.0560	1	5	250	Faint sp'tro'pic trace.	
10	0.0010	0.0560	1	10	250	" " "	

From the above it is plain (1–3) that, as was to be expected, strontium is incompletely precipitated by ammonium oxalate in slight excess and that its solubility is markedly lessened by increase of the precipitant. Furthermore (4–6), that calcium if present in quantity exercises a notable effect in promoting completeness of precipitation. Finally, that with very small amounts of strontium and a great excess of calcium the precipitation of the former is practically perfect in presence of a sufficient excess of ammonium oxalate, irrespective of considerable variations in the ammonium chloride. Additional experiments in which 5–6 grams of sodium chloride were added showed that this salt exercises a very slight but appreciable solvent effect on strontium oxalate. In entire absence of ammonium chloride on the other hand, precipitation of as much as 0.004 gram SrO is practically perfect in presence of 0.0560 CaO.

SECOND SERIES.

	Amount taken calculated as oxide.		$(NH_4)_2C_2O_4, H_2O$, Amount in excess of that required for conversion of total bases to oxalates.	NH_4Cl Grams.	Total bulk of solution. Cubic centimeters.	BaO in filtrate.	
	BaO	CaO	Grams.			Weight.	Percentage.
11	0.0509		½	5	250	0.0230	45.2
12	0.0509		1	5	250	0.0089	17.5
13	0.0509		2	5	250	0.0070	13.7
14	0.0509		4	5	250	0.0051	10.0
15	0.0509		½	10	250	0.0457	89.8
16	0.0509		1	10	250	0.0243	47.7
17	0.0509		2	10	250	0.0138	27.1
18	0.0509	0.0560	½	5	250	0.0436	85.6
19	0.0509	0.0560	1	5	250	0.0293	57.5
20	0.0509	0.0560	½	10	250	0.0489	96.0
21	0.0509	0.0560	1	10	250	0.0458	90.0
22	0.0509	0.0560	2	10	250	0.0463	90.9
23	0.0509	0.0560	4	10	250	0.0346	68.0
24	0.0509	0.0560	1	10	250	0.0206	40.5
25	0.0135	0.0560	1	5	250	0.0109	80.7
26	0.0135	0.0560	1	10	250	0.0106	78.5
27	0.00906	0.0560	1	5	250	0.0074	81.7
28	0.00906	0.0560	1	10	250	0.0079	87.2
29	0.00226	0.0560	1	5	250	0.00177	78.3
30	0.00226	0.0560	1	10	250	0.00197	87.2

In this series (11–17) the same action of precipitant and ammonium chloride that was observed in the first series makes itself manifest, only in much greater degree. Numbers 18–24 show in general the marked effect of small variations in the

amount of precipitant, although an exception may be noted in 22 when compared with 21. Comparison of 19 and 22 with 11 and 15 respectively shows that the presence of calcium exerts no retentive effect whatever on the barium, in marked contrast with its behavior toward strontium. With decreasing amounts of barium, the calcium remaining constant as well as the excess of precipitant, the slight influence of large variations in the ammonium chloride is apparent from numbers 25–30. The general result is to show conclusively that considerable amounts of barium may be separated almost completely from calcium by a single precipitation with ammonium oxalate in presence of considerable ammonium chloride, provided the precipitant is used in slight excess only.[1] Additional tests have shown that sodium chloride, as with strontium, slightly facilitates the separation from calcium; also that a double precipitation will effect the quantitative separation of over two mgms. BaO from fifty-six mgms. CaO under the conditions of experiments 29 and 30. In cases like the last the whole of the BaO has been recovered from the filtrates and from the calcium as nitrate no trace of barium could be separated by ether-alcohol. It goes without saying that by increasing the ammonium chloride still larger amounts of barium may be equally well separated, as has been proven by numerous tests.

In endeavoring to apply the knowledge thus gained to the separation of barium from both calcium and strontium, which is the problem usually encountered in silicate rock analysis, difficulties at once suggest themselves, namely, those arising from the partial solubility of strontium oxalate in ammonium chloride, from the presence of five to ten grams of fixed alkali salts, whereby the exact recovery of barium and the strontium that may have gone into solution with it is rendered much less certain, and furthermore, from the increased solubility of the oxalates of the calcium group when, as is very often the case, magnesium is present in some quantity.

Of several experiments made to test the degree of accuracy attainable, first in absence of sodium chloride, then in presence

[1] This fact was first observed by the writer in 1884, and was mentioned in a foot note to p. 592, appendix B., of Mr. S. F. Emmons' Monograph on the Geology and Mining Industry of Leadville.

of that salt and also of one of magnesium, thus reproducing the unfavorable conditions usually encountered in actual practice, the following will serve as fair examples.

1. CaO, 0.0560; BaO, 0.0023; SrO, 0.00095; $(NH_4)_2C_2O_4$, H_2O, one gram in excess, NH_4Cl, ten grams, total bulk of solution 250 cc. Two precipitations under precisely similar conditions. Found in filtrates, 0.00236 BaO, showing but the merest trace of strontium. Recovered from the lime, 0.00085 SrO holding fugitive spectroscopic traces of calcium and barium.

2. Precisely as in 1, with addition of $5\frac{1}{2}$ grams NaCl. In filtrates 0.0023 BaO, in lime 0.0006 SrO.

3. As in 2 with addition of 0.09 MgO. In filtrate 0.0023 BaO, in lime 0.0006 SrO.

It is apparent that the results are very satisfactory in 1, but that in 2 and 3 over thirty per cent. of the SrO has escaped detection although all the BaO was recovered. The amounts of both BaO and SrO taken in these tests exceed what is met with in the great majority of igneous eruptive rocks, and the error in SrO may therefore in most cases be disregarded, for after all an absolute error of twenty-five or even fifty per cent. in the estimation of a substance constituting only 0.1 per cent. of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

The procedure for the separation of the alkaline earth metals in silicate rocks as followed by myself with a fair degree of success for some time past, I will now outline, expressly premising, however, that it is not suitable for universal application, but that it seems to be the only one to meet the requirements of ordinary silicate analysis with anything approaching accuracy.

After a double precipitation, which should be made in any case, the ignited oxalate precipitate will contain nearly all the strontia and none of the baryta if the latter does not exceed 0.2–0.3 per cent. of the rock. If a larger quantity than 0.3 per cent. is present the precipitation by ammonium oxalate must be repeated or the rest of the barium subsequently separated from the strontium by ammonium chromate. The strontium is separated from the calcium by extracting the thoroughly dry nitrates (150–160° C.) by ether-alcohol, which is clearly shown by the

recent exhaustive researches of Fresenius[1] is the only one of the older methods at all capable of yielding a fairly satisfactory result. Hereby of course, any barium that might have been retained is also removed. The strontium weighed as sulphate should always be tested spectroscopically for barium, the barium sulphate likewise for strontium, either salt being brought into condition for making the test by reducing for a very few moments the whole or a part of the precipitate on a platinum wire in the luminous tip of the Bunsen burner, and then moistening with hydrochloric acid. If a trace of barium should be found with the strontium the error is insignificant and may be balanced by the strontium remaining with the calcium nitrate.

Before destroying ammoniacal salts, either by ignition or by nitric acid, prior to estimation of magnesia, a few drops of sulphuric acid should be added to precipitate the barium[2] which otherwise might contaminate the magnesium pyrophosphate. I say *might*, for small amounts of barium, up to 3 or 4 mgms. of oxide, will pass into the filtrate from the ammonio-magnesium phosphate. Only in exceptional cases have I ever found a trace of barium in the pyrophosphate after accidentally or purposely neglecting to effect a prior separation by sulphuric acid.

As to the barium itself it is improper to accept the amount thus separated from the magnesia as representing the total amount in the rock or mineral. It will almost always be found lower than the truth, probably for the reason that there are so many opportunities during the analysis for slight losses in the form of sulphate. Barium is best estimated in a separate portion which may also serve with advantage for the determination of titanium. The powder is decomposed in a capacious crucible with hydrofluoric and sulphuric acids, evaporation being repeated twice at least to ensure removal of all quartz. After volatilization of the excess of sulphuric acid the dry residue is digested with water containing several cubic centimeters of sulphuric acid to surely retain all titanium in solution, and a

[1] *Ztschr. anal. Chem.*, **29**, **30**, **32**, *1890*, *1891*, *1893*. Separation by amyl alcohol as recommended by P. E. Browning, *Am. J. Sci.*, **43**, 50, and 314, *1892*, has not been tried.

[2] The barium sulphate thus formed is not separated by filtration till after destruction of the ammoniacal salts, and, if this has been effected by nitric acid, not until after evaporation to dryness.

few drops of hydrochloric acid, and the solution is allowed to settle for some hours. The ignited insoluble matter is evaporated with relatively much sulphuric and a little hydrofluoric acid till the latter is removed and a clear solution results, which is then poured into a few cubic centimeters of cold water. The precipitate will now be free from calcium in all probability, but may contain a little strontium from traces of which it is easily freed by repeating once or twice the solution in strong acid and reprecipitation by water.[1] Unchanged weight after the final precipitation is evidence of purity of the barium sulphate, and the spectroscope should confirm this. These last mentioned manipulations require little expenditure of time even when they have to be repeated, and the result is usually eminently satisfactory. If the first weight of the barium sulphate is but one or two mgms. it is rarely necessary to purify the salt further.

Such is the procedure when only small amounts of barium and strontium have to be estimated. Should they be present in amount exceeding, say, two mgms. for SrO and four mgms. for BaO, or should with smaller contents a high degree of accuracy be desired, the already difficult analysis presents still greater difficulties. In such cases there remains no other way than to combine the barium and strontium found in the filtrates from the calcium oxalate with the strontium and barium separated from the oxalate itself, and to apply to the mixture the ammonium chromate method of separation as prescribed by Fresenius (*l. c.*). The practiced eye readily learns to judge by spectroscopic test of the ignited and weighed calcium oxide whether strontium is in sufficient quantity to necessitate this course, and the separate determination of barium as above described will decide with regard to that metal.

[1] If the rock happens to contain zircon this may, and probably will, remain with the barium sulphate until removed by appropriate means.

A PLEA FOR GREATER COMPLETENESS IN CHEMICAL ROCK ANALYSIS.[1]

By W. F. Hillebrand.

THE valuelessness to the mineralogist and geologist of many of the analyses of mineral substances made in earlier times is a fact too well-known to need substantiation. Defective methods of analysis, the difficulty of procuring pure reagents, and want of time for exhaustive examination have been largely responsible for this condition, but lack of appreciation of the fact, now so well established, that substances present in small amount may have an important bearing on the discussion of results, has no doubt contributed in no small measure to it.

Whatever the causes, the result has been the necessity for a vast amount of repetition in analytical work, and it behooves the present generation of chemists to heed well the warning and to work with a two-fold purpose in view, that of lightening the labors of those who come after us by enabling them to use our work with less supplementary examination, and of thereby enhancing our own reputations by meriting encomiums on work that has stood the test of time.

This monition applies to the lithologist as well as to the chemist, and the former should seek to make or have his analyses made as complete as possible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalies, and water; even going so far sometimes as to ask the chemist to omit tests for other constituents that may be present in small quantity for the sake of getting a greater number of more or less incomplete analyses accomplished. The latter, it is true, may serve the immediate purpose for which they were intended, but their incompleteness may on the other hand not only conceal points fruitful of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of total inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favor of greater completeness in rock and mineral analyses made for purely scientific purposes.

[1] Read at the Baltimore Meeting, December 27, 1893.

This is shown by the difference between the following analyses. The specimens were taken and analyzed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

	Earlier Analysis	Later Analysis
SiO_2	54.42	53.70
TiO_2	. .	1.92
Al_2O_3	13.37	11.16
Cr_2O_3	. .	0.04
Fe_2O_3	0.61*	3.10*
FeO	3.52*	1.21*
MnO	. .	0.04
CaO	4.38	3.46
SrO	. .	0.19
BaO	. .	0.62
MgO	6.37	6.44
K_2O	10.73	11.16
Na_2O	1.60	1.67
Li_2O	trace	trace
H_2O below 110° C	. .	0.80
H_2O above 110° C	2.76**	2.61
CO_2	1.82	. .
P_2O_5	. .	1.75
SO_3	. .	0.06
F	. .	0.44
Cl	. .	0.03
	99.58	100.40
Less O for Fl		.19
		100.21

Another instance of a similar kind is given below. Here again certain differences are explainable by natural variations

* From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

** In the published analysis it does not appear whether this is total water, or, as seems probable, only that remaining above 100° C.

in the proportions of the constituent minerals, but it can hardly be doubted that TiO_2, BaO, SrO, P_2O_5, and SO_3, were present in both specimens in approximately the same amounts. In the earlier analysis in this case determinations of some supposed unimportant constituents were purposely omitted or only made qualitatively, with results which cannot be otherwise than fatal to a full comprehension of the mineralogical nature of the rock.

	Earlier Analysis	Later Analysis
SiO_2	44.31	44.65
TiO_2	not est.	0.95
Al_2O_3	17.20	13.87
Fe_2O_3	4.64	6.06
FeO	3.73	2.94
MnO	0.10	0.17
CaO	10.40	9.57
SrO	. .	0.37*
BaO	. .	0.76
MgO	6.57	5.15
K_2O	3.64	4.49
Na_2O	4.45	5.67
Li_2O	. .	trace
H_2O below 110° C	0.77	0.95
H_2O above 110° C	. .	2.10
H_2O by ignition	3.30	. .
CO_2	. .	0.11
P_2O_5	. .	1.50
Cl	. .	trace
SO_3	. .	0.61
	99.11	99.92

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from my intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But I do maintain that in general the constituents which are likely to be present in sufficient amount to admit of determination in the weight of sample usually taken for analysis—say 1 gram for SiO_2, Al_2O_3, etc., to 2 grams for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative

* Not entirely free from CaO.

work, and their presence or absence noted among the results. If present in little more than traces that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavorable criticism when at some future time his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labor.

ELECTROLYTIC SEPARATIONS.

By Edgar F. Smith.

Received December 16, 1893.

FREUDENBERG published an article recently entitled "Über die Bedeutung der elektromotorische Kraft für elektrolytische Metalltrennungen" (*Zeit. für phys. Chemie.*, **12**, 97), in which are facts of great importance to all interested in the determination and separation of metals in the electro-chemical way. Some statements, however, have been made by Freudenberg to which I feel it my duty to reply. I discover upon p. 116, for example, these lines: "Auch gelingt eine Trennung (Kupfer) von Kadmium, welche bisher nur bei Gegenwart von Saltpetersäure möglich schien, vortrefflich, wenn man die Lösung mit 10–20 cc. verdünnter Schwefelsäure versetzt und mit einer Spannung von 2 Volt elektrolysiert. Das Kupfer wird rasch und völlig kadmium-freigefällt." This very separation was carried out successfully three years ago by Smith and Frankel (*Am. Chem. J.*, **12**, 104–112 and *Ber. d. chem. Ges.*, **23**, *Ref.* 413) as will be observed from the literature references and the examples that follow:

1. To a solution containing 0.1975 gram copper and 0.1828 gram cadmium were added ten cc. of sulphuric acid (sp. gr. 1.09) and then 100 cc. of water. A current that liberated 0.3 cc. of electrolytic gas per minute acted upon the above mixture for twelve hours. The precipitated copper weighed 0.1968 gram.

2. A second experiment made under analogous conditions, except that the volume of sulphuric acid equaled fifteen cc. gave 0.1975 gram copper.

Freudenberg, while recognizing the fact that Smith and Frankel by electrolyzing solutions of metallic double cyanides effected many separations, seems not to be fully acquainted with all that has been achieved in this direction. Thus upon p. 113 he speaks of the separation of mercury from copper and alludes to the early statement of Smith and Frankel that if the quantity of copper exceeded twenty per cent. of the mercury the separation would not be satisfactory. This is true, but if Freudenberg had examined the literature that appeared later from this laboratory he would have found that Smith and McCauley (*J. Anal. Chem.*, **5**, 489 and *Ber d. chem. Ges.*, **24**, 2936) observed that "it is not only possible to separate these metals (mercury and copper) completely when present together in equal amounts, but even when the quantity of the copper is twice that of the mercury. In brief, the separation is as readily and accurately made as that of any other metal, *e. g.*, zinc from mercury. Furthermore, the presence of zinc, nickel, or other metals, in no wise, influences the separation of mercury from copper." I welcome, therefore, the results of Freudenberg's experiments with mercury and copper as confirmatory of those published by Smith and McCauley.

The observation of Freudenberg (p. 114) relative to the removal of gold when precipitated directly upon platinum will be found to be antedated by reference to *J. Anal. Chem.*, **5**, 204.

As to the criticism made upon p. 117, in reference to the separation of bismuth from copper in the presence of potassium cyanide and citric acid I would only add that Smith and Frankel made numerous separations of these two metals in this way. Their results were highly satisfactory. It is true that

they never used quantities of bismuth exceeding 0.1 gram. The dishes in which the decompositions were made were large and offered ample surface so that the bismuth deposit was in every case satisfactory.

The separation of copper from arsenic, in ammoniacal solution, as outlined on p. 118 of Freudenberg's article, has already been successfully made by McCay (*Chem. Zeitung*, **14,** 509) and by Smith and Frankel (*Am. Chem. J.*, **12,** 428).

Again upon p. 122 Herr Freudenberg confirms an early observation made by Smith and Frankel in reference to their inability to completely separate cadmium from nickel in cyanide solution, but he is apparently ignorant of a later series of experiments by these same chemists in which they give proof that cadmium and nickel in cyanide solution can be separated in the electrolytic way if caustic alkali be added to the solution undergoing electrolysis. An example will illustrate:

A solution, containing 0.1723 gram cadmium, 0.1600 gram nickel, 2 grams of caustic potash, 2.5 grams of potassium cyanide to which 150 cc. of water had been added, was electrolyzed with a current that gave 2.2 cc. of electrolytic gas per minute. The precipitated cadmium did not contain nickel; it weighed 0.1723 grams (*J. Anal. Chem.*, **6,** 87, and *Ber d. chem. Ges.*, **25,** 784).

Freudenberg correctly adds on p. 124 that "Die Cyanverbindungen * * * * * * haben jedoch unsere Trennungs methoden bedeutend erweitert." This is evidenced by the many separations that have been effected in this laboratory in solutions of such compounds, *e. g.*

Cadmium from zinc, arsenic, tungsten, molybdenum, osmium, nickel, and cobalt; *gold* from palladium, platinum, copper, cobalt, zinc, and nickel; *mercury* from copper, zinc, nickel, cobalt, palladium, arsenic, tungsten, molybdenum, platinum, and osmium; and *silver* from copper, zinc, nickel, cobalt, arsenic, tungsten, molybdenum, platinum, and osmium.[1]

UNIVERSITY OF PENNSYLVANIA,
NOVEMBER 10, 1893.

[1] *Am. Chem. J.*, 11, 352, 264; **12,** 428; **13,** 417; *J. Franklin Inst.*, Dec., *1889*; *J. Anal. Chem.*, **5,** 489; **6,** 87.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

DETERMINATION OF NICKEL IN NICKEL-STEEL.

BY E. D. CAMPBELL.

Received December 21, 1893.

THE growing importance of nickel-steel has rendered it desirable to have a rapid and accurate method for the determination of nickel in that metal, since the value of the steel is largely dependent upon the amount of nickel which it contains.

The methods in use at present for the determination of comparatively small amounts of nickel in the presence of a large amount of iron, and the separation of the nickel from the manganese and copper, with which it is in most cases associated in this steel, involves usually one or more basic acetate precipitations and the use of either hydrogen sulphide or of ammonium sulphide in the subsequent work.

On account of the strong tendency of the basic acetate of iron to retain nickel, and of the various objections to the use of hydrogen sulphide or of ammonium sulphide as a precipitant, it was thought desirable, if possible, to devise a method which should not be open to any of the above objections.

The following methods worked out with my assistance by Messrs. Richard Fischer and W. G. Wallace, will, I think, be found to be sufficiently accurate for technical work. As the result of a large number of experiments upon solutions of steel, to which had been added known amounts of nickel, manganese and copper, the last two being added in amounts varying from two to ten times that in which they would occur in nickel-steel, in order that any interference of these elements might be detected, it was found that the nickel could be accurately determined within 0.001 gram, the usual error not exceeding 0.0003 gram to 0.0005 gram. The amount of nickel recovered is usually a little higher than the true amount, the increase being due to the solubility of ammonium manganous phosphate, the manganese of which accompanies the nickel in the subse-

quent work. The principles involved in the processes below described are the following:

1st. The iron is precipitated as ferric phosphate in cold, strong acetic acid solution, under which conditions it precipitates perfectly free from nickel, although retaining a small amount of copper.

2nd. The copper is separated from manganese and nickel in hydrochloric acid solution by means of granulated lead.

3rd. The manganese and lead, which displace the copper, are separated from the nickel by means of a cold ammoniacal solution of sodium phosphate.

4th. The nickel is determined in the ammoniacal filtrate from the phosphate of manganese and lead, by titration with standard potassium cyanide or by electrolytic deposition.

In case the nickel is accompanied by cobalt the latter metal remains with the nickel, and may be separated from it by any of the well-known methods after dissolving off the electrolytically deposited nickel.

The two methods described below are identical up to the point where a portion of the filtrate from the phosphates of manganese and lead is taken. The description of that part of the methods common to both will be first given, and then the two ways of treating the above filtrate for the final determination of nickel will be detailed.

DETAILS OF METHODS.

Take 2.2222 grams nickel-steel, place in a 500 cc. graduated flask, add twenty cc. nitric acid, sp. gr. 1.20, and five cc. strong hydrochloric acid sp. gr. 1.21. Boil until the solution is clear, which will usually require not more than from five to ten minutes. Remove from the plate and add 155 cc. sodium phosphate solution. If a slight precipitate should form which does not dissolve upon shaking, add carefully a few drops of hydrochloric acid until the solution clears up. Add twenty-five cc. strong acetic acid, sp. gr. 1.04 then 100 cc. sodium acetate solution, shake, dilute with water to 502.5 cc., shake again and allow to stand fifteen minutes. Filter through a dry, twenty-five cm. filter, catching the filtrate in a dry beaker. As soon as

enough of the filtrate has run through, which requires about ten minutes, draw off with a pipette 250 cc. of the filtrate, transferring to a number four beaker. This will give one-half of the solution, since it was found by experiment that the ferric phosphate from the amount of steel taken occupies 2.5 cc. Bring the solution to a boil and add twenty grams potassium hydroxide previously dissolved in forty cc. of water. Boil five minutes, then keep just below boiling point until the precipitate has settled and the solution is clear. This precipitates copper, manganese, and nickel so completely that the filtrate gives no color with hydrogen sulphide. Filter through asbestos, using a pump, decanting as much of the solution as possible before allowing the precipitate to get upon the filter. Wash with water. Dissolve the precipitate on the filter in a hot solution of six cc. strong hydrochloric acid with an equal volume of water. Wash the filter using only as much water as is necessary. To the solution in the flask, which should not exceed fifty cc. and should have a temperature of 40° to 50° C. add fifteen grams granulated lead and agitate at frequent intervals for five to ten minutes. This will completely precipitate the copper, a small amount of lead going into the solution. Filter through a small glass wool filter, catching the filtrate in a number two beaker; wash the granulated lead with a small amount of water and boil the solution down until it does not exceed sixty cc. Add ten cc. of sodium phosphate solution, then ammonium hydroxide until a precipitate just forms, then hydrochloric acid until the solution just clears up, cool until cold, and transfer to a cylinder or flask graduated to 111.1 cc. Add five cc. strong ammonium hydroxide, sp. gr. 0.90, dilute to the mark, shake well and allow to stand fifteen minutes. Filter through a dry nine cm. filter, receiving the filtrate into a dry beaker. Draw off, by means of a pipette, 100 cc. of this filtrate which is equivalent to one gram of the original steel, and treat by one of the two following methods:

I. ELECTROLYTIC METHOD.

Transfer the 100 cc. of filtrate above mentioned to a large platinum dish having a capacity of about 200 cc. Add twenty-

five cc. of strong ammonium hydroxide, sp. gr. 0.90, and dilute to 175 cc. Electrolyze for at least four hours, preferably over night, using a current yielding four cc. of electrolytic gas per minute. This strength of current can be easily obtained by connecting three medium sized cells. A very satisfactory arrangement to avoid the excessive loss of ammonia and the spattering of the solution due to the active evolution of gas, is to cover the platinum dish with a large watch glass perforated in the center through which the positive electrode, consisting of a large platinum cone, is suspended by means of a platinum wire.

The end of the precipitation of the nickel is indicated when a drop of the solution placed upon a drop of ammonium sulphide gives no color due to nickel sulphide. When the nickel is completely precipitated, disconnect the battery, wash the nickel thoroughly with water, then finally twice with alcohol and, after draining off as much as possible, heat for a few minutes in an air-bath at 110° C. Cool and weigh. After getting the combined weights of the platinum dish and nickel, dissolve off the latter by warming with 5–6 cc. of nitric acid, sp. gr. 1.20, then wash the platinum dish by means of water and alcohol and dry and weigh as before. The difference in the two weighings gives the nickel.

It is more satisfactory to weigh the empty dish after the precipitated nickel has been dissolved off than before electrolysis, since in this way a shorter time will elapse between the two weighings and consequently less error will be introduced from variations in atmospheric conditions. This latter source of error may be still further reduced by employing as a counterpoise for the platinum dish, upon which the nickel is precipitated, a similar platinum dish washed, dried and cooled under the same circumstances as the former.

2. VOLUMETRIC METHOD.

Take 100 cc. of the filtrate from the phosphate of manganese and lead, add hydrochloric acid very carefully until the blue color of the double ammonium nickel chloride disappears, then add ammonium hydroxide, drop by drop, until the blue just reappears and add an excess not exceeding one cc. Dilute to 200

cc., add five cc. of cupric ferrocyanide indicator and run in standard potassium cyanide until the solution turns from the purple color of the indicator to a perfectly clear light straw yellow. Subtract from the number of cubic centimeters of potassium cyanide used, the correction for the indicator. The difference gives the amount necessary to convert the nickel into the double cyanide of potassium and nickel. Multiplying this by the factor of the potassium cyanide, expressed in metallic nickel, gives the amount of nickel in one gram of the original sample.

SPECIAL APPARATUS AND REAGENTS.

500 cc. graduated flask with an additional mark at 502.5 cc. 250 cc. drop pipette. 100 cc. drop pipette.

Glass stoppered cylinder or flask graduated to 111.1 cc. The graduated apparatus should be carefully calibrated and compared before using.

Sodium phosphate solution, made by dissolving 200 grams of the ordinary crystallized disodium hydrogen phosphate in 1860 cc. of water. Ten cc. of this solution contain one gram of the crystallized salt, and it requires seventy cc. to precipitate one gram of iron as ferric phosphate.

Sodium acetate solution, made by dissolving 250 grams crystallized sodium acetate in 820 cc. of water. 100 cc. of this solution contain twenty-five grams of sodium acetate, which is a slight excess over that which is necessary to convert the nitric and hydrochloric acids to sodium nitrate and chloride, with the liberation of the corresponding amount of acetic acid.

Granulated lead is of the same quality as that used in assaying. In size it should be that which passes through a sieve with twenty meshes to the inch, but remains upon a sieve with forty meshes.

Before using, the lead should be washed with dilute hydrochloric acid (one part acid to two parts water) in order to dissolve any oxide that may be present.

Standard nickel solution. This may be made from chemically pure nickel by dissolving 2.5 grams nickel in fifty cc. nitric acid, sp. gr. 1.20, adding an excess of hydrochloric acid, evaporating on a water-bath nearly to dryness, then diluting to 1000

cc., one cc. equals 0.0025 gram nickel. Or it may be made from chemically pure nickelous chloride by dissolving six grams in water with the addition of a few drops of hydrochloric acid, and diluting to 1000 cc. This latter solution must be standardized. In order to do this, take thirty cc., place in a large platinum dish, add twenty-five cc. of strong ammonium hydroxide, dilute to 175 cc. and electrolyze as in the electrolytic method for nickel.

Standard potassium cyanide solution. Take twelve grams of chemically pure potassium cyanide, dissolve in water, dilute to one liter. This must be standardized against a standard nickel solution. Since the presence of ammonium salts interferes somewhat in the titration with potassium cyanide, necessitating the use of a slightly greater amount of potassium cyanide than would be required if there were no ammonium salts present, it is better that the potassium cyanide be standardized under the same conditions as are met in analysis. To standardize the potassium cyanide, take 15–20 cc. of standard nickel solution, add six cc. of hydrochloric acid, sp. gr. 1.20, ten cc. sodium phosphate solution, ammonium hydroxide until the solution turns blue and then five cc. in excess. Now add hydrochloric acid until the blue color of the double nickel chloride disappears, then again ammonium hydroxide until the blue just reappears, and an excess not exceeding one cc. Dilute to 200 cc., add five cc. cupric ferrocyanide indicator, and run in potassium cyanide until the solution changes from the purplish color imparted by the indicator to a perfectly clear light straw yellow.

Divide the amount of nickel in the standard nickel solution taken by the number of cubic centimeters of potassium cyanide used, less the correction for the indicator. The result will give the strength of the potassium cyanide expressed in metallic nickel.

Cupric ferrocyanide indicator. Take 2.5 grams of crystallized cupric sulphate, dissolve in twenty-five cc. of water, add to this a solution of ammonium oxalate until the precipitate first formed just redissolves, then dilute to 500 cc. Dissolve 2.5 grams of potassium ferrocyanide in 500 cc. of water, then slowly pour this solution into the cupric sulphate solution, stirring constantly

during the operation. This will give a deep purplish brown solution of cupric ferrocyanide which may precipitate partially on standing; but the precipitate so formed will be so fine that it will easily remain in suspension for a long time, upon shaking the bottle, thus insuring uniform composition. To find the correction for the indicator take 200 cc. of water, add 6–8 drops of ammonium hydroxide, then five cc. of indicator, taken after shaking the bottle well, and then run in potassium cyanide until the characteristic change of color is obtained.

Five cc. of cupric ferrocyanide of the above strength require from 0.15–0.2 cc. of potassium cyanide, one cc. of which is equivalent to 0.0025 of nickel. If a stronger end reaction is desired, ten cc. or even fifteen cc. of the indicator may be used and a suitable correction made.

Repeated analyses of steel have shown that the nickel may be determined, by the volumetric method, within from 0.0003 to 0.0005 gram of the true nickel content, duplicate determinations being made in three hours. The electrolytic method requires three hours to the time the solution is ready for electrolysis.

ANN ARBOR, MICHIGAN.
December 7, 1893.

PRELIMINARY REPORT OF THE COMMITTEE ON THE TARIFF.

THE COLUMBIAN UNIVERSITY,

WASHINGTON, D. C., January 15, 1894.

H. W. Wiley, Ph.D., Etc., Etc.,

President American Chemical Society,

Sir:—Your favor of January 5, 1894, announcing the appointment of the Committee on the Tariff, with the undersigned as Chairman has been received, and while from the nature of the case, it has not been possible to call the committee together for action, steps have been taken to secure information upon which to base our action.

We learn that efforts are being made to try and settle the question "What are philosophical or scientific instruments and prepa-

rations?" and in this particular we would call attention to the fact that in 1884 the Secretary of the Treasury referred this very question to the National Academy of Sciences, and that the Committee appointed by that body reported that an instrument is "philosophical," not in consequence of its special construction or function, but in consequence of the uses to which it is to be put, and that many instruments may be put both to uses which are philosophical and to uses which are purely industrial or commercial, it therefore appears to this committee that the terms "philosophical apparatus and instruments" should be held to cover all such instruments and apparatus imported for the purpose of improving natural knowledge. (*Rept. Nat. Acad. Sci.*, 66–67; 1885.)

From inquiry thus far of officials familiar with the operation of our tariff laws it appears that the difficulty in securing for educational institutions the full advantage of paragraph 667, page 47 of the Tariff of October 1st, 1891, arises from the fact that if dutiable articles used in commerce or the industries be admitted duty free for educational institutions the door is thrown open for the evasion of the law by those not entitled to the benefit of the Act.

It has been suggested by experts that this difficulty might be surmounted and that educational institutions might obtain that relief which Congress evidently intended they should have, by substituting for the present statute one providing that educational and other favored institutions be granted a rebate of duties on all dutiable goods and material consumed by them. In this case goods would be purchased directly from the "stock on hand" of dealers, or by advanced orders as heretofore, and when delivered the invoices would be accompanied by authenticated statements of the duties paid, which amounts would be returned on presentation of the statement to the Secretary of the Treasury or to his authorized agent. It is claimed that by this plan the delays now incident to purchase, and the difficulties arising from inconsistent appraisement will be remedied.

Your committee would respectfully ask that any who are interested in this matter should send their views and suggestions to the chairman of the committee and especially that they should

supply him with the particulars of any instances of failure of the act or inconsistencies in appraisements which may have come personally to their notice.

Respectfully submitted,

CHARLES E. MUNROE,
Chairman.

EXPERIMENTS ON THE ESTIMATION OF GRAPHITE IN PIG METAL.

BY FRANK L. CROBAUGH.

Received December 19, 1893.

THE determination of graphite in pig iron is often required. At furnace laboratories there is rarely time and equipment necessary to do this work by combustion. Appended are some details of experiments made in the search for a simple, yet accurate, method. In all cases counterpoised two 9 cm. filters were folded together and the filtration performed upon them. After partial unfolding and drying at a temperature not exceeding 100° C., (higher temperature chars paper after treatment) the excess of weight of the inner paper will be the weight of the graphite or graphite plus impurities. If now the paper containing graphite plus impurities (chiefly silica) be burned and the residual weight subtracted from the excess of weight of the inner paper, the difference may be graphite. Five grams of the same drillings were taken for each operation.

The metal contained 1.68 per cent. silicon. The washing in every instance was first with water and hydrochloric acid 1.1 sp. gr. until all iron was removed. The last washings were invariably with water. When there was intermediate treatment on the filter, it will be described with the experiment. In duplicate experiments, A and B, 125 cc. nitric acid, 1.135 sp. gr. was used as solvent and continued at gentle heat for one hour.

	A	B
Weight graphite plus silica . . .	0.2105	0.2500
Weight of residual silica	0.0255	0.0658
	5)0.1850	5)0.1842
	3.70	3.68

The larger amount of silica in B is due to its standing at a gentle heat while A was being filtered. This strength nitric acid dissolves the most silicon according to Dr. Drown, but our experience has been that it separates on slight evaporation or on standing.

In duplicate experiments C and D, 60 cc. hydrochloric acid 1.1 sp. gr. was used as a solvent.

After complete solution 100 cc. of water was added to each and allowed to stand over night.

	C	D
Weight graphite plus silica	0.3500	0.3489
Weight of residual silica	0.1732	0.1721
	5)0.1768	5)0.1768
	3.53	3.53

The larger amount of silica separated rendered the burning of the graphite more difficult than in A and B. The amount of silica separated represents nearly all the silicon of the metal.

In experiment E, the solvent was 125 cc. nitric acid sp. gr. 1.135 added first, then immediately 12 cc. of Baker and Adamson's 40 per cent. hydrofluoric acid. Solution was perfect within five minutes at a gentle heat, after which the solution was boiled vigorously for five minutes longer, being constantly kept covered to prevent evaporation.

	E
Weight graphite plus silica	0.1768
Weight of residual silica	0.0000
	5)0.1768
	3.53

It was thought that hydrofluoric acid would either cause more of the silicon to go into solution and remain there or volatilize it from the boiling acid.

Some glaze was taken from the beaker but no severe corrosion occurred in several treatments in the same beaker.

Intermediate washing with a mixture, one-third strong ammonia and two-thirds water, was made with the hope of dissolving any silica that might still cling to the graphite.

On burning the filter containing the graphite nothing was left in the crucible but some minute dark spots, (likely traces of

elements seldom estimated in pig iron) too slight to effect the determination in question. In experiments A, B, C, and D, I feared that the silica weighed with the graphite might be hydrated and thus give too high results in graphite.

Experiment E provided means for eliminating this objection by wholly freeing from silica. Thus far no attention has been paid to the extraction of combined carbon from the graphite, except as far as the solvents used would do this work, either by dissolving and retaining it, or evolving it. When the graphite of experiment E was washed with ammonia, after all iron was removed, brownish coloration appeared in the funnel tube during the first two washings which suggested combined carbon in some form dissolved in ammonia. The following experiments were all started exactly the same as was E. The washing will be described along with results given.

	F	G
Weight graphite plus silica . . .	0.1818	0.1800
Weight of residual silica	0.0000	0.0000
	5)0.1818	5)0.1800
	3.63	3.60

Both F and G were washed with alcohol, ether, and ammonia in order. Each of the three washings brought the brownish coloration as noted in E.

	H	I
Weight graphite plus silica . . .	0.1820	0.1855
Weight of residual silica	0.0000	0.0025
	5)0.1820	5)0.1830
	3.65	3.66

H was washed with ammonia only. Copious brown color came. I was washed with alcohol and ether only. Brown color came.

	J	K	L
Weight graphite plus silica	0.1878	0.1830	0.1790
Weight of residual silica	0.0000	0.0000	0.0000
	5)0.1878	5)0.1830	5)0.1790
	3.75	3.66	3.58

J was also washed with alcohol and ether only. Brown color came. K was washed with alcohol, ether, and ammonia, in or-

der named as were F and G. It was observed that more color came with ammonia than with alcohol and ether. The alcohol-ether and ammonia filtrates of K were preserved and will receive attention later. L was washed with ammonia, alcohol, and ether in order. Scarce a trace of color came with alcohol and ether.

In none of these experiments except I, was any residue left in the crucible except the dark spots previously alluded to, (soluble in boiling hydrochloric acid sp. gr. 1.20) and in that case, residual silica, showing that ammonia may be necessary to dissolve the last traces of silica, but not always necessary as proven by J.

From a comparison of results and character of washings, it is evident that ammonia is certainly as efficacious a wash as alcohol and ether for removing combined carbon or its compounds, and that where ammonia is used, alcohol and ether are unnecessary. The variation of the hydrofluoric acid results is not so great as to be inadmissible from a commercial standpoint.

This variation may be due to errors of manipulation, or to small graphitic crystals or nuggets crumbled rather than drilled from the pig and larger than the remainder of drillings thus rendering the sample of drillings not homogeneous.

These interlaced spongy particles of graphite, sometimes three mm. on a side are often noticed after solution of pig in 1.135 sp. gr. nitric acid. It may also be due to small amounts of fine graphite penetrating the inner paper and being retained by the outer paper or penetrating it also.

This phenomenon is sometimes noticed especially where retained by the second paper thus giving a dark color. Finally the chemical or mechanical action of the filtration may have disturbed the equality in weight of the two papers. Why then setting aside these sources of error and the dark spots on the crucible are we not weighing pure graphite, if the analysis be conducted as typified in experiment E? This modus operandi is shorter and free from the perplexities of the caustic potash method of Karsten. The alcohol-ether filtrate from K was evaporated to gentle dryness and formed a black mirror-like residue on the beaker, completely soluble in the ammonia wash

when warmed gently. The residue from the ammonia filtrate presented the same appearance but was not soluble in alcohol and ether, but readily taken up by ammonia.

Both filtrates on evaporation threw out the dissolved matter in brownish flocks. We hope to investigate this point more thoroughly and also the action of ammonia on the total carbon of pig iron as obtained by use of the double chlorides. Such work may aid in obtaining a better knowledge of the forms of combination of carbon with iron and the forms in which it is separated under different conditions.

Attention will also be paid to the character of spots on the crucible, but these would not be common to all pig iron and might exist to a greater extent in some than in others. I may note in conclusion that all filtrations were performed by aid of the pump, and that more closely concordant results might have been obtained had the filtrations been performed upon asbestos. It would also be interesting to determine whether the silicon of the metal under this treatment is volatilized or largely in solution.

LABORATORY OF STEWART IRON CO., L'T'D.,
SHARON, PA., DECEMBER, 1893.

THE DETECTION OF STRYCHNINE IN AN EXHUMED HUMAN BODY.[1]

BY W. A. NOYES.

PROFESSOR T. G. Wormley in his book on the Micro-Chemistry of Poisons states that strychnine has never been found in an *exhumed* human body after a longer period of burial than forty-three days. His authority is the Ann. d'Hyg., April, *1881*, 359. I have not been able to find in any chemical journal a contradiction of this statement, though there is a statement in the old edition of *Watt's Chemical Dictionary* which seems to be inconsistent with it. Under these circumstances the following account of a recent toxical case may be of some interest.

On April 26th of this year Drs. W. L. Athon and O. Mitchell, of Marshall, Ill., brought to me for examination the stomach, liver and a portion of the intestines of a child who died on June

[1]Read at the Baltimore Meeting, December 28, 1893.

23rd, 1892, and was buried the following day. The body was exhumed on April 25th, 1893, after a burial of 308 days. The material submitted for examination weighed 505 grams. About fifty grams were examined for arsenic and other mineral poisons with negative results. About 350 grams of the remainder were extracted with dilute sulphuric acid and alcohol by the usual methods. The aqueous residue which remained on concentration of the alcoholic solution contained a considerable amount of oily matter which was separated by filtration and washed as thoroughly as possible. This residue (A) is usually considered to be nearly free from alkaloids but it was further examined as described below.

The filtrate, after concentration, treatment again with alcohol etc., was rendered alkaline with caustic soda and extracted with chloroform. The chloroform left, on evaporation, a considerable amount of oily bases which were partly volatile, as was shown by their fumes with hydrochloric acid. To separate the strychnine from this residue it was heated on a water-bath with a little concentrated sulphuric acid for two hours. After neutralizing the acid, the solution was extracted with chloroform. The residue obtained, was treated again in the same manner, and that residue, again. Stoehr[1] has shown that when pure strychnine is heated to 100° with pure concentrated sulphuric acid, for some time, it is completely converted into the mono-sulphonic acid. Apparently in the presence of much foreign matter and with a small amount of acid in an open watch-glass a considerable portion, at least, of the strychnine escapes this action of the acid. In any case, a portion of the last residue referred to above gave with potassium pyrochromote and sulphuric acid the violet color, changing after a short time to an onion red, which is characteristic of strychnine. While the use of concentrated sulphuric acid is open to objection and should never be resorted to when it is possible to avoid it, I do not know of any other method which would be successful in the case of such residues and such minute amounts of strychnine as were obtained in this case.

The oily residue (A) was treated with some purified ligroin,

[1] *Ber. d. chem. Ges.*, 18, 3429.

and very dilute sulphuric acid and the mixture was filtered with the aid of a pump in such a manner that both acid and ligroin were drawn through the filter. The acid solution and the ligroin were then separated and the strychnine was recovered from the solution and purified essentially as before. A considerably larger amount was obtained from this portion than from the first. The strychnine obtained was identified by the characteristic reaction with potassium pyrochromate and sulphuric acid, by the intensely bitter taste, by the crystalline form and double refraction as seen with the microscope, by the crystals obtained from the chloride with potassium chromate, and by the effect of about $\frac{8}{10}$ of a milligram upon a frog weighing about two grams. The frog died from the effects of the poison, the symptoms of tetanus being fully developed within ten minutes after the dose was administered. The crystals of the chromate were chiefly of the branching forms; there was a little evidence of octahedra but they were not positively identified. The branching forms, however, developed the characteristic violet color when touched with concentrated sulphuric acid.

The total amount of strychnine recovered was estimated to be about two milligrams.

In the trial, the chemical evidence was not contested. The defendant was, however, acquitted on other grounds.

ROSE POLYTECHNIC INSTITUTE,
DECEMBER 23, 1893.

NOTES ON DETERMINATION OF NICKEL IN STEEL.[1]

BY JOSEPH WESTESSON, CHEMIST TO THE WASHINGTON NAVY YARD.

THE desirability of being able to determine nickel in steel by means of a shorter process than the one, now mostly in use, gave me cause some time ago, when a number of samples from nickel-steel plates were submitted for analysis to the ordnance laboratory, and when the tediousness of the said process became particularly apparent, to make some investigations in order to find a more direct method, and I shall beg permission to mention in a few words, what my trials led to.

In the process, above mentioned, the nickel is precipitated

[1] Read by title at the Baltimore meeting, December 28, 1893.

by means of hydrogen sulphide in the acetate solution, obtained by separating iron from nickel; the sulphide is filtered off, dried, ignited, dissolved in aqua regia and converted into the double sulphate with ammonia in order to obtain a suitable solution for electrolysis.

It occurred to me, that there ought to be some way, by which the nickel could be electrolytically precipitated *directly* in the acetate solution, and thus that part of the procedure, embracing the precipitation with hydrogen sulphide, entirely eliminated. If this could be done, it is evident, that there would be quite a saving of time, besides doing away with an unpleasant feature of the method. It became, therefore, my aim to simplify the old method in this peculiar part.

Now, as the presence of chlorides will prevent the electrolysis of nickel, and as the separation of the iron from nickel always had taken place in a chloride solution, I decided to bring my original solution into the shape of sulphates and then proceed on the old lines. After having made a number of more or less successful trials, I finally came to the conclusion, that the following method would answer the purpose very well:

One gram of the sample is dissolved in twenty cc. of sulphuric acid of 1.16 sp. gr., and the solution kept boiling for some time, whereupon five cc. of weak nitric acid is added in small portions. The solution is now evaporated until all the nitric acid is expelled, allowed to cool, water added and heated until clear. Neutralization with carbonate of soda is done in the usual way, but care should be taken not to carry it too close to the point of neutralization. Add water so as to make the bulk 375-400 cc. and precipitate with acetate of soda; filter into a casserole and evaporate the filtrate over a moderate flame; redissolve the ferric precipitate and repeat the precipitation twice, taking care not to make the bulk more than 400 cc. each time, and adding each filtrate to the first one. When the filtrates have been evaporated down to 400 cc., add ten cc. of concentrated ammonia and boil for a few minutes. The manganese will then settle out, evidently as H_2O_2MnO, and is filtered off, whereupon the filtrate is ready for electrolysis. If the ammonia should be added to the concentrated filtrates, when *cold*, the manganese

will not separate out but will interfere considerably with the electrolysis later; it will in that case not only settle out at the anode, but will in fact contaminate the nickel on the cathode, not as loosely settled dioxide but alloyed with the nickel. When on the other hand, the manganese is precipitated by ammonia in the hot solution, the nickel is to a small extent carried along with the manganese, but I have in all my experiments never found the nickel, lost in that way, amount to more than one to one and a half per cent. of the amount of nickel present in the steel.

How this modification of the old process compares with the original a few results will show.

In a nickel-steel, containing 3.50 per cent. nickel, determined by the old process, the amount found by the modified process in five different analyses was: 3.42 per cent.—3.51 per cent.—3.48 per cent.—3.51 per cent.—3.43 per cent., and in another steel containing 0.19 per cent., the following amounts were found: 0.18 per cent.—0.19 per cent.—0.19 per cent.

The time necessary for analysis of this kind I have found to be about eight hours. Thus, if the analysis is commenced at 8 A.M. the solution will be ready for electrolysis at twelve o'clock, or before; with seven or eight Grove cells in good condition the analysis should be concluded at 4 P.M. I have invariably commenced at noon and left my cylinder over night on four Grove cells, the separation of iron from nickel being completed about four o'clock, or sometimes a little later.

A CORRECTION.

By H. L. Payne.

Received January 29, 1894.

IN the *Journal of Analytical and Applied Chemistry* for September, *1892*, **6**, No. 9, I published 'A method for the Preparation of a Standard Iodine Solution,' and on page 482 I have taken the molecular weight of two atoms of iron as 128 instead of 112. This singular error which vitiates the entire calculation following it, has been called to my attention by several readers and I desire to correct the mistake and again call attention to the method itself. If any one has been unfortunate

enough to take the figures just as I gave them, he has no doubt been disappointed with the method. To such I make a humble apology and ask that they try again using the following changes.

The relation between the iron and the sulphur value of a permanganate solution is 112 to 32 or 7 to 2 instead of 8 to 2 and of a phosphorus permanganate solution with an iron value 6,141,285 cc. should be taken to make one liter of iodine solution titrating 0.01 per cent. S on five grams iron, instead of 325.7 cc.

To make the whole matter clearer I may state the process of computation in a more general form making use of the atomic weights 56.00 for Fe and 32.06 for S. To make an iodine solution titrating exactly 0.0001 gram S per cc.—0.01 per cent. S per cc. on one gram of substance taken—divide 349.34 by the iron value, *i. e.*, the grams per liter or milligrams per cc., of the permanganate solution to be used. This gives the number of centimeters of such a solution to be used in making one liter of iodine solution. If more than one gram of substance is taken, multiply the number accordingly; thus for a permanganate solution whose iron value is 0.005 gram Fe per cc., take 69.87 cc. to one liter, or if five grams of iron or steel be used in the sulphur determination, take 349.34 cc. per liter.

The reactions in the foregoing method are as follows:

$$K_2Mn_2O_8 + 10FeO + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2O_3$$

$$K_2Mn_2O_8 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 10I.$$

$$5H_2S + 10I = 10HI + 5S.$$

therefore $K_2Mn_2C_8 = 10Fe = 10I = 5S$,

or $2Fe = S$.

I hope now that this method has been correctly presented to the readers of THE AMERICAN CHEMICAL JOURNAL, that it will be made of the service which I believe its simplicity and accuracy deserves. I have tried it for over three years and have never had the slightest trouble.

CITY LABORATORY,
CLEVELAND, OHIO.

A RAPID AND ACCURATE METHOD OF DETERMINING THE MOISTURE AND OIL IN LINSEED CAKES AND OTHER FEEDING STUFFS.[1]

By A. P. Aitken, D.Sc., Chemist to the Highland and Agricultural Society of Scotland.

IT frequently happens that when the same sample of linseed cake is analyzed by different chemists very considerable differences occur in the proportions of oil and moisture found by them.

The explanation of these discrepancies is to be found, not only in the different methods employed, but also in the inconstancy of the results obtained by the same method.

Determination of Moisture.—As regards the determination of moisture, the common practice in this country is to expose one or two grams of a finely ground sample in a water-bath for two hours and to regard the loss of weight as the measure of the moisture. A recent examination of this method has shown me that it may be very inaccurate and that uniform results cannot be obtained by it.

The amount of heating which a sample gets in an ordinary water-bath during two hours may not be sufficient to deprive it of all its moisture. The temperature within the bath is not constant and it is always below 100° C. The temperature of the external air, the amount of ventilation, the frequency with which the door is opened, the quantity of the sample used, the nature of the vessel containing it whereby a greater or less amount of surface is exposed to the current of hot air, are all fluctuating conditions. Moreover, in the case of linseed cake the sample continues to absorb oxygen during the whole time of its exposure in the bath and it does so the more rapidly the higher the temperature and the greater the surface exposed.

It thus happens that when a sample of finely ground linseed cake is exposed in a water-bath it goes on losing weight from loss of moisture for a time and thereafter gains weight from ab-

[1]Read before the World's Congress of Chemists, August 22, 1893.

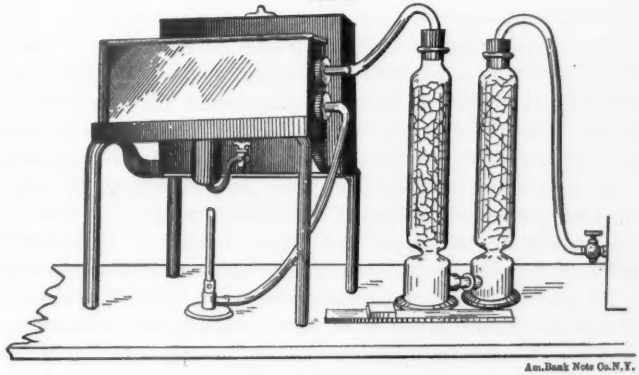
sorption of oxygen. Therefore, the time at which the sample ceases to lose weight is not that at which the sample is dry but only the time at which the loss of moisture and the gain of oxygen counterbalance each other.

In order that the sample may be thoroughly dried and that it may at the same time suffer no oxidation, it must be dried in an atmosphere from which air is excluded. An atmosphere of hydrogen is excellent for the purpose, but one of coal gas does quite as well and it is most readily obtainable. I have used coal gas for the purpose for some years and it is used also in some of the continental laboratories.

The apparatus I am about to describe secures that the sample is dried exactly at the temperature of boiling water and is so constructed that the coal gas is heated to that temperature before it comes in contact with the sample. It may be made of any dimensions, but the size which I prefer is that described below and capable of drying eight samples in an hour and a half.

The apparatus consists of a small rectangular box, ten inches long, four inches deep, and two inches wide, placed on edge as shown in Fig. 1, and in sections longitudinally and transversely, Fig. 2, A.

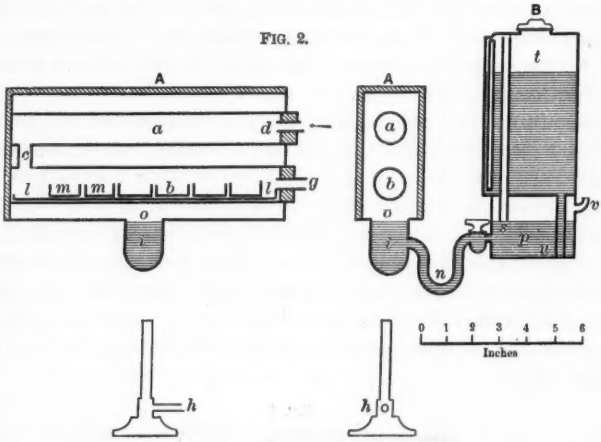
FIG. 1.



Through the box from end to end pass two hollow cylinders made of telescope tubing, and soldered into the box at each end.

The box is simply a steam-bath to heat the two tubular chambers, which are fitted at one end with the perforated corks and have the other end either closed with corks or entirely soldered up as in the diagram. The upper tubular chamber *a* is for heating the gas, and the lower one *b* for drying the samples, which are contained in little aluminum boats *m m* resting on a carrier of brass *l l* which slides into the chamber.

FIG. 2.



These boats, capable of holding one or two grams of cake, weigh only about one to two grams each, and are, therefore, very well adapted for weighing small quantities. The gas from the tap is led first through two drying bottles, filled, one with soda-lime and one with chloride of calcium, and enters the apparatus by the tube *d* in a perfectly dry state. It passes along the upper chamber *a*, where it is heated, and then through *c*, which is a tube connecting the upper and lower chambers. It arrives at the lower chamber *b* both hot and dry and passes along, drying on its way the samples (usually one gram each) contained in the little aluminum boats *m m*, eight of which can be accommodated on the carrier. The gas leaves the apparatus by *g*, and may be burnt there, but as the flow of gas is sufficient to keep a small Bunsen going, I connect the tube *g* with the Bunsen *h*.

The flame of this little Bunsen keeps the water in the thimble-

shaped cup *i* briskly boiling. The water in the thimble (about 1–2 ounces) is kept constantly at the level *o* by its connection with the automatic cistern B connected with the bath by the tube *n*, which is bent downwards and up again so as to prevent hot water from passing back into the lower section of the cistern *p*. As soon as the level of the water in this lower section falls below the mouth of the tube *s*, a bubble of air passes up the tube into the upper cistern *t*, and a corresponding quantity of water flows into the lower section through *u*, and restores the level of the water. A small hole *v*, into which an upwards bent tube is fitted, allows air to enter the lower section. The object of the upturned tube is to prevent water from spilling out of the air-hole, when the apparatus is carried about. This cistern contains more than a day's supply of water, and gives no trouble, and is supported along with the bath, on a light iron frame as shown in Fig. 1. The inside of the bath is thus constantly full of steam, which escapes by a hole at the top about $\frac{3}{16}$ of an inch in diameter. The bath is made of copper, but its entire surface is protected against contact with the surrounding air by means of asbestos sheeting $\frac{1}{8}$ inch thick.

The temperature in the upper chamber is thus kept constantly at the boiling-point of water, and not several degrees below it, as is usually the case in even the best water-baths. By means of this small apparatus, eight one-gram samples of cake can be dried within two hours. They are removed by drawing out the carrier, transferred to an exsiccator, and weighed in the aluminum trays, whose weights are known and deducted, thus giving the moisture. The results are perfectly accurate, and the cost in gas is very small — only about one cubic foot per hour.

The samples are now ready to have their oil extracted and estimated.

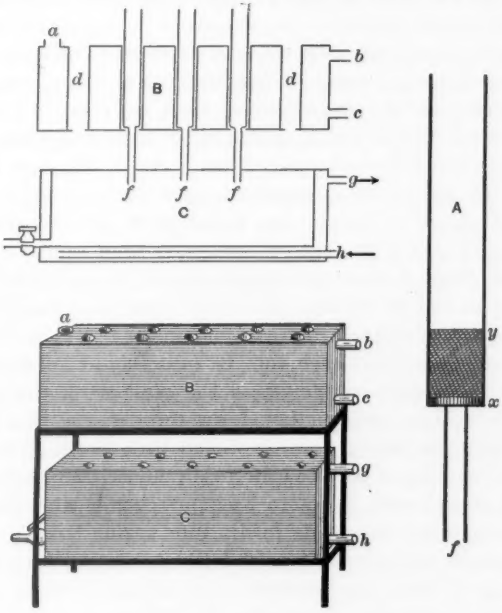
It is not essential that the last traces of moisture should be removed before the oil is extracted. If the sample is dried for half the time required to completely dry it, it is in a suitable condition for oil extraction. Nine-tenths of the moisture will have gone by that time, and the presence of about one per cent. of moisture does not appreciably affect the amount of oil extracted.

I prefer to take the samples whose moisture I have estimated, and which are completely dry, because I have a method of extracting oil by which even very small quantities of oil can be accurately estimated, and which possesses the further advantage of being more rapid than any other method that I know of.

Solvent for Oil in Cakes.—Ether, bisulphide of carbon, or benzene, are the solvents usually employed, but as ether is the one which is most common, most rapid, and most comfortable to work with, I prefer it to the others. It is a little more expensive, but the quantity used in oil determinations is small; the additional cost is more than compensated by the advantages mentioned. Ordinary pure ether, as supplied by wholesale chemists, having a specific gravity of 0.73, is sufficiently pure and dry for the purpose of oil extraction; but as most of the ether used is recovered by redistillation in the laboratory and may contain water, it must be dried before being again used. This is sufficiently accomplished by shaking it up with chloride of calcium repeatedly for some days, and redistilling.

Determination of Oil.—The oil may be determined either by directly weighing the oil extracted, or by weighing the dried substance before and after the oil is extracted, and determining the oil by the difference of the two weighings. There are two objections to the former method. In the first place, the flask in which the oil is caught is itself very heavy and presents too great a surface; and in the second place, the evaporation of the residual ether in the drying chamber takes a long time, and the surface of the oil becomes covered with a thin pellicle due to oxidation. The latter method is much to be preferred if a suitable apparatus can be had for doing the work simply and rapidly. The apparatus I have devised for that purpose is very simple, and is shown in Fig. 3. It consists of a set of brass tubes, polished smooth inside, see Fig 3, A, which is half the actual size, and is represented as charged with the dried sample. In charging the tube, the first thing required is to drop into it a small disk of wire gauze x, and then to insert a single or double wad of filter-paper, which is cut to fit the tube tightly, and pushed home with a ramrod. (I use a cork borer of the proper size for cutting the wads, and a piece of glass rod flattened out at the end

while hot, as a ramrod.) The object of the wire-gauze disk is to facilitate the flow of the ether through very fine powders, such



as ground grain, and also to enable the sample to be removed from the tube more easily after the oil is extracted. In the case of oil cakes the wire-gauze disk may be dipensed with.

The sample is then poured in through a little metal funnel whose neck just fits the extraction tube. Any powder adhering to the funnel is brushed in with a camel-hair brush, then another wad *y* is patted in on the top of the sample, carrying with it any powder that might have adhered to the side of the tube and leaving the upper part of the tube clean and bright. The tube is now put into one of the holes in box B, which is simply a warming box made of zinc, shown also in section.

The holes *d d*, etc., are tubes which pass through the box from top to bottom, and are made a shade wider than the ex-

traction tubes, which should drop in easily. As soon as the extraction tubes are filled they are dropped into these tubular openings, which are provided with a ledge at the base to sustain the extraction tubes.

Hot water is poured into the box at *a*, or a constant current of hot water may be made to flow through the box, entering at *b* and flowing out at *c*, by attaching these by means of tubes to a copper coil under which a Bunsen is burning at a safe distance. At first I used the circulation method, but now I prefer to have no gas burning anywhere near the extractor. It is quite convenient to supply hot water at *a*, and withdraw the cooled water at *c* from time to time. As soon as the extractor tubes are dropped into their places, ether is poured into them to within an inch of the top, and by the time that the five tubes are thus filled the ether will be boiling in the first tube. A cork is now firmly fixed into each tube in succession, thus preventing the ether-vapor from escaping, and the presence of the confined vapor, forces the boiling ether down through the samples and out through the lower opening *f* into little bottles placed beneath, so that the oil may be collected from each tube separately. If the oil of each tube is not to be kept separate, the mouths of the extractor tubes are made to dip into a zinc box C beneath, through small holes on the top, and there the oily ether collects and is run off from time to time, and redistilled for future use. There is considerable loss of ether by this method, but that is much reduced as one becomes expert in handling the apparatus; and if the other box below is provided with double walls between which a current of cold water is kept flowing through the openings *g*, *h*, the loss from evaporation is still further reduced.

This process of filling the tubes with ether is repeated ten, fifteen, or even twenty times, according to the difficulty of extracting the oil. The operation is complete when a drop or two of ether, falling from the exit *f* towards the end of an extraction, is caught on a clean watch-glass and evaporated without leaving any residue. The extractor I use in my laboratory is fitted for ten tubes, and after a little practice the oil from the ten samples of cake can be extracted with it in one hour. The extraction of oil from a sample, by means of Soxhlet's apparatus, which is the

one chiefly used at present, takes about five hours, so that this little apparatus has a great advantage over it as regards speed; but many comparative tests have proved that it also has the merit of making a more thorough extraction of oil. This is due to the fact that the extraction is made with boiling ether, and that no oily ether that has once been washed through is able to run back upon the sample again, as is the case with Soxhlet's apparatus. In extracting the oil from some substances, such as grain or other starchy powders, the resistance to the passage of ether is so great that even a tightly-fitting cork is apt to be blown out by the pressure of the vapor. In such cases I use caps with a cork washer inside, which fit on to the top of the tubes with a screw of half a turn which is very rapidly adjusted.

When the oil has been completely extracted, the removal of the sample is a neat and easy operation. It is done by inserting the cut end of the glass ramrod into the opening *f* and slowly pushing out the sample (wads and all) into a weighed aluminum capsule. The wads are now removed, after brushing off any particles of powder adhering to them with a camel-hair brush, and the dry powder, after exposure for a short time to a temperature of 100° C., is cooled in an exsiccator and weighed. The difference between that and the former weighing, is the weight of the oil extracted.

It is evident that the accuracy of the oil determination by this method depends upon the accuracy of the determination of the moisture; but as by the method above described the moisture can be accurately determined, there is no danger, if that method is adopted, of making any error in the estimation of the oil. In estimating moisture in the ordinary way it is considerably underestimated, usually to the extent of one-twentieth or more, and in such circumstances that which is underestimated in the moisture is usually added to the oil; for the common practice is to determine the percentage of moisture in one part of the sample, the percentage of moisture and the oil together in another, and to subtract the former from the latter, so as to give the percentage of the oil.

It thus happens that in the analysis of an ordinary linseed

cake differences of two or even three per cent. are not unusual in the percentage of oil found by different analysts.

I have submitted this method to a long series of tests in my laboratory during the past winter and I have been so satisfied with the accuracy and uniformity of the results obtained by it and with the simplicity and rapidity of the whole process that I cordially recommend it to agricultural chemists in America and especially to those who have small laboratories and a large number of samples to analyze.

The apparatus is not costly and I hope the description I have given of it is sufficiently clear to enable it to be easily understood and imitated.

ON THE DETERMINATION OF NITRATES IN POTABLE WATER.

By Augustus H. Gill.

Received January 16, 1894.

PART I.

THE remark of Tiemann,[1] that the estimation of no other substance has so constantly occupied the attention of the analytical chemists of the last decade to the extent to which the determination of nitric acid has engaged (literally "enchained") them, will, I think, be appreciated by all those who have worked upon the subject. Perhaps no determination requires more care, or occasions more trouble in its execution, or is more unsatisfactory when finished, than the one in question.

There are two general modes of procedure:

a. The direct estimation, and

b. The reduction to ammonia.

a. DIRECT ESTIMATION.

The direct processes which have been found to give the best results are those of Schulz-Tiemann,[2] Schloesing-Reichardt,[3] Crum-Lunge,[4] and Marx-Trommsdorf.[5] These are only appli-

1 Tiemann Gaertner "Wasseranalyse" 3rd. Ed'n., p. 168.

2 *Ber. d. chem. Ges.*, **6**, 1041.

3 *Ztschr. anal. Chem.*, **9**, 24.

4 *Phil. Mag.*, (3), **30**, 426.

5 *Ztschr anal. Chem.*, **9**, 171.

cable where relatively large amounts of nitrate are to be estimated, over 0.6 parts of nitrogen as nitrate per 100,000, and even with this quantity two or three hundred cc. of the water must be evaporated for use. This concentration is objectionable as it offers an opportunity for the oxidation of nitrites and their decomposition with loss of nitrogen,[1] and also for the oxidation of organic matter, and where many determinations are to be made it is very troublesome.

There is too, a decided advantage in estimating the nitrogen contents *immediately upon receipt of the sample, and if possible, upon the water as received.* This has been pointed out by Tidy[2] in reference to the carbon contents of a water, and applies with still greater force to the nitrogen which is more susceptible to change.

Another direct method is the phenolsulphonic acid process; it originated with Sprengel[3] and apparently fell into disuse until it was again brought to notice by Grandval and Lajoux.[4] Since then articles upon it have appeared by Fox,[5] Johnson,[6] Lindo,[7] Smith,[8] Bartram,[9] and Hazen and Clark.[10]

The two latter have criticised the process severely, and it seems to me unfairly, and it was with the idea of seeing how far

1 $NH_4NO_2 = 2H_2O + N_2$.

2 *J. Chem. Soc.*, **35**, 53 and 97.

3 *Pogg. Ann.*, **121**, 188.

4 *Compt. rend.*, **101**, 62.

5 *Tech. Quarterly*, **1**, 1.

6 *Chem. News*, **61**, 15.

7 *Chem. News*, **58**, 1, 15, 28.

8 *Analyst*, **10**, 197.

9 Bartram, *Jour. Frank. Inst.*, March 17, 1891, has published an article entitled "A Source of Error in the Determination of nitrates in Water by the Phenolsulphonic Acid Process," in which he says it was found that the phenolsulphonic acid undergoes a change after preparation. As ordinarily prepared, it may possibly undergo a change to the para acid; any difficulty is now obviated by the use of the pure disulphonic acid. I think the method has been submitted to an unusually severe test, 0.5 parts of nitrogen to 20 parts chlorine being very rarely met with in water analysis. It is unadvisable to estimate nitrates higher than 0.1 as it cannot be done with accuracy. Possibly the nitrate solution itself may have varied. I have solutions which contained 1 part of nitrogen as nitrates per 100,000 and which in the course of seventy-two hours showed but 0.04 part, and in ninety-six hours none whatever. Another containing 4.5 parts, showed at the end of six days but 0.25 part.

10 *J. Anal. Appl. Chem.*, **5**, 1.

their critique could be supported by experiment that this investigation was undertaken.

The process consists in evaporating the water,—usually ten cc.,—to dryness in a porcelain dish, treating the residue with phenolsulphonic acid, diluting with water and neutralizing with ammonia. In presence of nitrates, ammonium picrate is formed, the color of which is matched by standard solutions of potassium nitrate which have been treated in like manner.

One of the principal objections is the formation of the three nitrophenols "the principal products being the ortho and para *mono* nitrophenol." This cannot be the case: according to Richter,[1] in the presence of a large excess of strong sulphuric acid—as we have here—the nitration goes farther, forming the di and tri-substituted compound. Granted, however, that the different amounts of these compounds were formed, it would be exceedingly anomalous to have under exactly the same conditions, at one time a large quantity of dinitrophenol formed, and at another time a large quantity of the trinitro body. Furthermore, the readings given in their comparative table of the various nitrophenols are probably incorrect; it has been found impossible to read colors as deep as 1.2 parts nitrogen per 100,000 in an eight inch tube more closely than twenty-five per cent.

The suggestion of one of them,[2] of making up standards in eight inch tubes and allowing them to stand "for months," has been found to be of no advantage, as a very decided deterioration does take place. The other suggestion, of making up standards by dilution of a solution obtained by treating a large quantity of potassium nitrate, is open to the objection that the colors produced are not the same as those from making up each one in a dish separately. In this connection I would remark that the same holds true of the colors produced by the Nessler reagent; for example, ten cc. of standard ammonium chloride is made up to 100 cc. and the reagent added. The colors produced by diluting one cc., five cc., or ten cc. of this (colored) solution to fifty each are not the same as those obtained by diluting 0.2

[1] *Lehrbuch d. Org. Chemie.*, 5th Ed'n., 572.

[2] Hazen, Report Mass. State Board of Health. "Purification of Sewage and Water," *1890*, 712.

cc., one cc., or two cc. of the standard ammonium chloride solution each to fifty cc. and adding the Nessler reagent, but in every case darker.

The process is dismissed with the remark: "We have not been successful in so controlling the reaction as to get a constant product." The chief agents in the action of nitric acid upon any compound are heat and concentration. If, therefore, the dishes containing the residues are always at the same temperature,—which they must be, being at the temperature of the room—and the acid used of the same composition, it is difficult to see how the results could fail to agree in every case, and direct experiment proves this to be so, equal quantities of pure nitrate solutions agreeing exactly.

The investigation was conducted with reference to the following points.

I. ACIDS.
   a. Various acids.
   b. Method of treatment.
   c. Quantity of acid used.

II. EVAPORATION.
   d. Effect of sodium carbonate.
   e. Temperature at which it is carried on.
   f. Quantity evaporated.
   g. Effect of chlorine.

III. COMPARISON WITH STANDARDS.

The preparation of the phenolsulphonic acid is a matter of first importance, and for which, strange to say, no one has ever given definite directions. Kekulé[1] found when phenol and sulphuric acid were mixed, according to the temperature, varying amounts of ortho and para phenol monosulphonic acids were formed. As these could not fail to influence the action upon the dry-water residue, an acid of perfectly definite composition,—the pure disulphonic acid $C_6H_3OH(SO_3H)_2$, probably $OH : SO_3H : SO_3H = 1 : 2 : 4$, which with nitric acid gives *picric acid even in the cold*,[2]—has been mostly used in these experiments.

This is prepared as follows: three grams of phenol of good quality and thirty-seven grams of pure sulphuric acid sp. gr.

[1] *Ztschr. fur Chemie*, 10, 199.

[2] Kekulé Lehrbuch III, 236.

1.84 (Kahlbaum's synthetic phenol and Baker and Adamson's "Strictly Pure" sulphuric acid were usually employed) are mixed in a flask and heated for six hours *in, not upon*, a water-bath to 100°.

To determine the number of sulphonic groups, a portion of this mixture was neutralized with barium carbonate, lixiviated with water, filtered, the filtrate evaporated and the barium salt recrystallized, giving handsome orthorhombic prisms. A determination of barium in this gave 35.16 per cent., the theory requiring 35.22 per cent. A determination of water of crystallization gave 15.66 per cent., theory, 15.62 per cent. H_2O. The acid as thus prepared may crystallize out upon standing, it being rather insoluble in the strong sulphuric acid, in which it forms supersaturated solutions. It may be brought into solution by reheating a short time, or by dilution with a small quantity of water, the undiluted acid has always been used.

The experiments were performed as follows: Two solutions were employed, one containing in one cc., 0.1000 part of nitrogen per 100,000 as potassium nitrate; the other in addition to this seven parts chlorine as sodium chloride per 100,000. Of these, portions of one cc. each were measured out and diluted to five and ten cc. with distilled water and evaporated in porcelain dishes.[1]

The $2\frac{1}{2}$ inch evaporator containing the water residue was moistened with ten drops—0.7 cc.—of the phenolsulphonic acid, and by rubbing with a short glass rod every part of the residue covered with it; seven cc. of water are now added,—measured in later experiments by a Vanier[2] overflow pipette,—the solution stirred and three cc. ammonium hydrate, measured in like manner, added, the solution again stirred to insure uniformity, and the rods removed. In many cases the colors could be compared directly in the dishes, but in case of doubt the comparison took place in tubes about $1\frac{5}{8}$ inches deep and $\frac{5}{8}$ inch in diameter.

[1] A convenient way of marking these dishes is to remove a small patch of the glaze upon the outside of the dish by glass etching ink, leaving a rough surface for the lead pencil.

[2] *J. Anal. Chem.*, **2**, 145.

Each determination is the average of at least two closely agreeing determinations.

All results are stated in parts per 100,000.

I. ACIDS.

(a) VARIOUS ACIDS.

Equal parts of phenol and sulphuric acids.	The colors obtained were brown and an accurate matching was impossible.
Unknown mixture of ortho and para sulphonic acids from five per cent. solution of phenol.	The colors obtained were fairly good, but in some cases were reddish tinted.
Pure ortho phenol monosulphonic acid.[1]	This gave a precipitate with the ammonia and the colors were all bluish-green tinted.
Pure disulphonic acid, 7½ per cent. solution.	The colors obtained were a pure yellow and did not change upon standing. This, therefore, gives the best results.

(b) METHOD OF TREATMENT.

At 100°.—Sprengel[2] states that the residue should be nearly at 100° when treated. Experiments performed by treating the residues upon the steam-bath with the cold acid and also with the acid at 100° gave no better results than those obtained in the ordinary way.

At 0°.—Treatment of the chilled residues upon ice with ice-cold acid gave decidedly lower results than those obtained in the usual manner, the nitration probably not going as far.

Addition of substances.—The addition of phenol or phenolsulphonic acid to the water before evaporation is of no advantage whatever.

(c) QUANTITY OF ACID USED.

If chlorine be absent or in small quantity, the amount of acid used makes very little difference. Enough should be used to cover the residue readily, usually ten drops=0.7 cc. is sufficient. For example, with equal quantities of the same nitrate solution which should have given a reading of 0.1000, the following results were obtained:

[1] Prepared by the cold evaporation in vacuo of the officinal solution of Merck's "Aseptol" and subsequent solution in sulphuric acid.

[2] *Pogg. Ann.*, 121, 188.

TABLE I.

Showing the effect of the quantity of acid used.

Without Chlorine.		With Chlorine, seven parts.	
10 drops acid.	6 drops.	10 drops acid.	6 drops.
0.0925	0.9000	0.0750	0.0700.

It is evident then that the use of too little acid causes the loss of nitric acid.

II. EVAPORATION.

It is well known that certain salts in solution undergo decomposition when boiled. Fittig[1] found this to be true of ammonium chloride, Debbits[2] of several acetates with loss of acetic acid, and with the nitrate, sulphate, acetate and oxalate of ammonium with loss of the respective acids. Leeds[3] and Fox[4] have shown that nitrates are volatile at 100° and even lower temperatures.

In order to ascertain what the influence of the evaporation really was, the following experiment was tried:

An intimate mixture of dry finely powdered potassium sulphate and nitrate was made by grinding them together in an agate mortar for several hours. Sixteen portions of 100 milligrams each were accurately weighed out, each containing about 0.072 milligram of potassium nitrate. Twelve portions were dissolved each in ten cc. of water, four of these evaporated at 100°, four at 65°, and the remaining four at 20° over sulphuric acid.

TABLE II.

Showing loss of nitrate by evaporation at various temperatures.

	Dry.	20°.	65°.	100°.
I	0.1000	0.0890	0.0900	. . .
II	0.1050	0.1000	0.1080	0.1160

The readings varied among themselves by 0.0200 and hence were averaged.

To obviate this variation, sixteen portions of one cc. each of a nitrate solution were measured out, nine cc. of water added and all allowed to evaporate over sulphuric acid at a temperature of 20°. Ten cc. of water were added to each one of twelve of

[1] *Ann. Chem. Pharm.*, **128**, 189.

[2] *Ber. d. chem. Ges.*, **5**, 820.

[3] *Am. J. Sci.*, (3) **7**, 197.

[4] *Tech. Quarterly*, **1**, 1.

these and four evaporated at 20°, four at 65°, and four at 100°; this gave a series in which exactly the same amount of nitrate in every case was spread uniformly over the dishes and had been subjected to these various temperatures.

TABLE III.

Showing loss of nitrate by evaporation at various temperatures.

Dry	20°	65°	100°.
0.1000	0.0990	0.0965	0.0990

These results indicate that there is a loss of about one per cent. when the water is allowed to evaporate at ordinary temperatures over sulphuric acid, or in a steam-bath where it evaporates rapidly and is *immediately* removed; at 65° where the evaporation is slower, and the time of exposure to heat consequently lengthened, the loss is greater, in this case about three and a half per cent.

(b) EFFECT OF SODIUM CARBONATE.

With a view of fixing the nitric acid and thus diminishing the loss by evaporation, it has been suggested that carbonate of sodium be added to the water before evaporation; as carbon dioxide is given off upon treatment with acid, it is possible that this carries off with it a slight quantity of nitric acid. Ten portions each of nitrate solution, the reading of which should have been 0.1000, were evaporated, the average reading was 0.0970, with the addition of soda 0.0973. Ten portions each of the same solution, containing in addition seven parts chlorine per 100,000, when similarly treated gave 0.0821, with the addition of soda 0.0812.

The avidity of acetic acid being much less than that of nitric acid, added to the fact that it was non-volatile at the temperatures employed, led to the suggestion that some of its salts be employed as a substitute for the sodium carbonate. Sodium acetate when added to the water, gave rather lower results than those obtained when it was not used.

(c) TEMPERATURE AT WHICH EVAPORATION IS CARRIED ON.

The accompanying table shows clearly the effect of temperature upon the determination.

The solutions should have all read 0.1000 part nitrogen as

potassium nitrate per 100,000, they were all treated with carbonate of sodium and each figure represents the mean of two closely agreeing determinations.

TABLE IV.

Effect of temperature.

Pure niter solution.

	Quantity evaporated.		
Temp.	1 cc.	5 cc.	10 cc.
100°.	0.0925	0.0920	0.0920
65°.	0.0890	0.0890	0.0880
20°.	0.1050	0.0980	0.1000

Niter solution with 7.0 parts chlorine.

	Quantity evaporated.		
Temp.	1 cc.	5 cc.	10 cc.
100°.	0.0680	0.0700	0.0600
65°.	0.0650	0.0650	0.0680
20°.	0.0935	0.0920	0.0700

It is evident that there is a decided loss of nitrate when evaporation takes place at 65° (the temperature which water assumes in a porcelain dish when upon the top of a water-bath) over that lost at 100° and here even over that lost at 20°. With chlorine this is even more perceptible; the reason for the increased loss at 65° is probably, as already stated, that the time of exposure at this temperature is longer.

It is important, however, that the dishes be removed as soon as dry, as the subsequent exposure causes loss of nitrate.

TABLE V.

Effect of heat upon the dry residue.

Water contained 0.1000 part N as N_2O_5, 7.0 part Cl.

	Quantity evaporated.		
	1 cc.	5 cc.	10 cc.
Removed at once	0.0750	0.0710	0.0740
Exposed half an hour at 65° . .	0.0700	0.0625	0.0690

(f) QUANTITY OF SOLUTION EVAPORATED.

The quantity of solution evaporated seems to exercise but slight influence upon the results, although the smaller it is, the less the loss; this is evident from all three of the preceding tables.

(g) EFFECT OF CHLORINE.

The presence of large quantities of chlorides in the water does

unquestionably lower the results. If the process be conducted in the usual way, by the evaporation of ten cc. at 100° it shows in Table IV, a loss of from thirty to forty per cent. of nitrogen as nitrate. If a smaller quantity, five cc. or even one cc., be used, and the evaporation be carried on at 20° over sulphuric acid, this loss is reduced to six or seven per cent., and of this probably one half is due to unavoidable errors in matching the colors.

If the chlorine amounts to but 2.0 parts per 100,000, which is perhaps high in waters of doubtful character, it exercises practically no influence.

TABLE VI.

Effect of 2.0 parts of chlorine (as NaCl) per 100,000. Readings should be 0.1000.

	1 cc.	10 cc.
100°.	0.0900	0.0900 (average of five determinations.)
65°.	0.0900	0.1000
20°.	0.0975	0.1050

III. COMPARISON WITH STANDARDS.

The yellow color of the picrate solution when as high as 0.1000 is extremely hard to match accurately; the tints must be read off at once without any delay as the difficulty increases with the time spent in comparison. It is well after reading perhaps a dozen, to rest the eyes by looking intently at a piece of blue paper.

As a result of a long series of experiments upon three different people,—all experts in the comparison,—it was found that the error of reading colors up to 0.0500 part N as N_2O_5 was 0.0020 or 0.0030; up to 0.1000 part N as N_2O_5 was 0.0050.

No advantage was gained by the use of colored glasses or, when the colorimeters were used, of colored papers underneath them.

The process does not, as stated by Grandval and Lajoux,[1] and also in Graham-Otto,[2] estimate the nitrogen present as nitrates; this is clearly impossible, as the action of nitrous acid upon phenolsulphonic acid results in the formation of nitrosophenol

[1] *Compt. rend.*, 101, 62.

[2] *Lehrbuch d. anorgan. Chem.*, 2, Part 1, 200.

$C_6H_4 \begin{matrix} NO \\ OH \end{matrix}$ which is colorless in dilute solution. This view was supported by an experiment with pure sodium nitrite prepared from pure silver nitrite, in which no color whatever was obtained upon treatment with the phenolsulphonic acid.

The results of this paper may be summarized as follows:

The most satisfactory manner of execution is,—in the case of a water high in nitrates,—to use that quantity which will give a reading of about 0.0700 when one or two cc. are employed; in the case of ground water ten cc. of a portion which has been decolorized by the use of alumina in the cold, is evaporated upon the water-bath, the dish being placed in the steam and removed *as soon as dry*, or better, when a drop is still remaining. In case the chlorine be high, which often accompanies high nitrates, this evaporation had best take place in vacuo over sulphuric acid, and the chlorine, if it exceeds 7.0 parts per 100,000, removed by silver sulphate which has been proved to be free from nitrate.[1]

In case one or two cc. of the water is used the 0.7 cc. of acid used is sufficient to cover the residue completely.

The error of reading up to 0.0500 is 0.0020 or 0.0030, four to six per cent. Up to 0.1000 is 0.0040 or 0.0050, four to five per cent., but the process as here described is more trustworthy, delicate and accurate than any process yet published.

For easy comparison 0.720 gram KNO_3 can be dissolved in one liter of water, ten cc. of this allowed to evaporate in vacuo, treated with acid, made up to a liter and portions as wanted made alkaline with ammonia, of this ten cc.=0.1000 part nitrogen as potassium nitrate per 100,000.

Acknowledgment.—The writer would hereby acknowledge his indebtedness to Prof. Drown and Mrs. E. H. Richards, chemists to the Massachusetts State Board of Health, for hints and suggestions, and to Miss Isabel F. Hyams and Mr. H. C. Tuttle, also of the Board of Health staff, for valuable assistance in making many of the readings involved in the preceding work.

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[1] Samples from E. Merck, marked "C. P." contained enough nitrate to vitiate all results.

EXPERIMENTS ON THE ANALYSIS OF PIG COPPER, BRASSES AND BRONZES.

By James S. de Benneville.

Received January 17, 1894.

In a recent number of this Journal (January, 1894) a preliminary note was given on a method for systematic examination of pig copper and high copper percentage alloys. It is proposed in this paper to present some of the experiments involved in the work of which the note was a résumé. The results are familiar to those working in copper analysis, but on taking up the subject I was not able to find in the literature accessible to me quantitative data of many current statements. It is known for instance, that in determining tin in copper alloys by solution in nitric acid that phosphorus and arsenic remain in their oxidized forms with the metastannic acid but it was sought to ascertain whether the reaction was quantitatively exact or whether phosphorus and arsenic were still to be looked for in the filtrate from the residue.

Taking up tin the question was as to how that metal alloyed with copper reacted during analysis. The usual method of determining tin in such alloys is by solution in nitric acid, evaporating off excess of acid, diluting and when the precipitate has settled, filtering. The points to be taken into consideration are: 1. Whether or not the metastannic acid formed is soluble in nitric acid. Experiment answers this negatively. 2. Whether or not the metastannic acid is soluble in ammonium hydroxide, ammonium nitrate, or both. Experiment answers this also negatively. 3. The state of purity in which the residue is obtained. It is a matter of experience that in nitric acid solution, especially when evaporated to a point where basic salts are liable to form, the stannic oxide is found to be more or less contaminated with such salts of copper, manganese, and iron. These impurities adhere most tenaciously and washing with dilute nitric acid will not remove them completely. The reaction of tin phosphate and arseniate holds quite rigidly. The attack on tin by nitric acid is a solution and conversion into

an oxidized form and in this reaction if phosphoric or arsenic acids be present the stannic phosphate or arseniate is formed which, like the bismuth salts, is insoluble in nitric acid of five per cent. or less strength. The importance of this reaction in copper analysis is very great. With the exception of certain special alloys the tin present will generally exceed the quantity necessary to hold the arsenic and phosphorus in an insoluble form and the phosphate and arseniate of tin are not readily decomposed by simple digestion with alkali sulphide (S_n) but require fusion.

The following experimental results were obtained. Expressed in grams or fractions thereof. The term "metastannic acid" is used to indicate the residue obtained on dissolving tin in nitric acid, but such residue also contains stannic acid.

I. Solubility of the metastannic acid or residue obtained on dissolving pure tin in nitric acid. Excess of acid removed by evaporation to pasty condition. Dilution forty cc. Filtered after twelve hours.

Tin taken	1368	1544	1610	1744	1623	1674
Tin found	1365	1557	1620	1745	1630	1683

II. Solubility of the metastannic acid or residue obtained. Dissolving the tin in excess of nitric acid. Present 6.92 free nitric acid. Dilution 150 cc. Filtered after twelve hours.

Tin taken	1812	1734	1795	1808	1746
Tin found	1812	1738	1792	1800	1732

III. Solubility of the metastannic acid or residue obtained. Dissolving in nitric acid. Evaporating to paste. Diluting to forty cc. and digesting twelve hours with five grams ammonium nitrate.

Tin taken	1963	1822	1763	0600	1814	1280
Tin found	1965	1842	1784	0602	1839	1301

IV. Solubility of the metastannic acid or residue obtained. Conditions as in III. Digesting twelve hours with 6.52 NH_3.

Tin taken	1653	1472	1785	1530	1671	1242
Tin found	1679	1498	1808	1563	1690	1260

V. Solubility of metastannic acid or residue obtained. Conditions as in III and IV. Digesting twelve hours with five grams NH_4NO_3+6.52 NH_3.

Tin taken	1495	1527	1357	1731	1567	1511
Tin found	1534	1567	1408	1784	1606	1546

VI. Precipitation of tin by NH_4HO. Five grams of copper present 6.92 free HNO_3. Ammonia added at once to re-solution of the copper salt. Filtered after twelve hours. All contaminated with copper oxide. Washed with dilute nitric acid.

Tin taken	1986	1770	1779	1928	1977
Tin found	2095	1907	1866	1998	1958

VII. P_2O_5 remaining with metastannic acid. Excess of tin present. Phosphor-tin treated with nitric acid. Evaporated to paste. Dilution forty cc. Present 0.0631 phosphorus in one gram.

Phosphor-tin taken	3150	2580	2763	2400	0990
P in filtrate	0003	trace	trace	0004	trace
Per cent. P in residue	99.905	..	..	99.983	..

VIII. P_2O_5 remaining with metastannic acid. Excess of phosphorus present. Conditions as in VII. Present 0.0250 phosphorus.

Tin present	0078	0076	0067	0077	0075
P combined	0190	0146	0131	0151	0154

The ratio of SnO_2: P_2O_5 is 1 : 4 (on averaging).

IX. As_2O_5 remaining with metastannic acid. Excess of tin present. The arsenic and tin treated with nitric acid. Conditions as in VII. Present 0.0067 arsenic.

Arsenic in filtrate	0012	0009	0011	0012	0011
Per cent. As in residue	83.5	86.6	83.6	83.6	83.6

X. As_2O_5 remaining with metastannic acid. Excess of arsenic present. Conditions as in IX. Present 0.0134 arsenic. In filtrate.

Arsenic	0129	0121	0129	0107	0113
Per cent. loss	3.73	11.19	3.73	20.15	15.67

In both IX and X tin and arsenic were attacked by nitric acid in presence of each other. In IX there was a large excess of tin (0.1000 gram). In X there was 0.0095–0.0110 tin present. The operations were conducted in the same manner and repeated.

XI. Phosphate of tin with metastannic acid. Digested at 70° for five hours with excess Na_2S.

Phosphorus present	0071	0046	0069	0061	0136
P as unconv'd phosphate	0024	0018	0041	0037	0114
Per cent. unconverted	33.8	37.1	59.4	60.3	83.8

No. 5. (83.8) in solution in nitric acid was inadvertently carried to complete dryness.

XII. Arseniate of tin with metastannic acid. Digested at 70° for five hours with ammonium sulphide. Filtered from residue after twelve hours. Present 0.0067 arsenic.

As as unconv'd arseniate . .	.0051	0057	0055	0058	0057
Per cent. unconverted . . .	76.12	85.07	82.09	86.56	85.07

The residue, acids of tin, were converted by ignition in a porcelain crucible, to stannic oxide. The full heat of a Fletcher lamp was used. Phosphorus was precipitated by molybdic solution and weighed as $Mg_2P_2O_7$. Arsenic was weighed as $Mg_2As_2O_7$.

With antimony a number of similar experiments were carried out. The antimony was weighed as Sb_2O_4 and Sb_2S_5.

XIII. Solubility of the residue obtained by dissolving pure antimony in dilute nitric acid (1-3) evaporated to pastiness. Dilution forty cc. Filtered after twelve hours.

Antimony taken	1004	1186	1198	1243	1120
Antimony found	0947	1151	1170	1232	1017

XIV. Residue as in XIII. Nitric acid solution containing 6.92 free nitric acid. Diluting 150 cc. Filtered after twelve hours.

Antimony taken	2214	2166	2244	2600	2277
Antimony found	2046	1829	2079	2537	2160

XV. Residue as in XIII. Digested twelve hours with 6.52 NH_3. Dilution forty cc.

Antimony taken	1012	1000	1584	1278	1100
Antimony found	0982	0965	1551	1272	1038

XVI. P_2O_5 remaining with the oxides of antimony on solution of metallic antimony in nitric acid. Excess of antimony present. Evaporated to pastiness. Diluting forty cc. Present 0.0051 phosphorus.

Phosphorus in filtrate . .	0020	0033	0018	0018	0015
Per cent. P in residue . .	60.78	25.29	64.70	64.70	70.59

Antimony is a most troublesome determination to make in copper analysis. If it can be separated and obtained in a precipitate of small bulk the solubility of the sulphide in alkali sulphide can be taken advantage of, but to apply this reaction in

the presence of ten to twenty grams of copper in the form of an easily oxidized sulphide is a difficult and tedious operation.

The object of the use of ammonia and barium hydrate is to effect for copper what is done in iron analysis for single determinations. In separating manganese or phosphorus in a steel, one of the objects is to retain the iron in solution, precipitating out the element which is present only in small quantities. The bulk of the copper being held in solution by the ammonia and precipitation being completed by barium hydrate the analysis of a pig copper is simplified by having a small precipitate to work upon. An excess of barium hydrate being used the separation of the crystalline barium carbonate probably has its effect in the filtration. If we have to make a systematic examination of a copper alloy, as in any case the residual tin oxide obtained by the nitric acid method would have to be purified, it is easier to do this work of purification and separation in such a way as to obtain quantitative results of the different minor constituents sought. If there is enough iron, tin, etc., to fix all the phosphorus and arsenic in an insoluble form the results are quantitative for these elements. To add ferric chloride to obtain such results may be of advantage, but iron is an important object of search in such examination and these two elements are not difficult to separate from the main bulk of copper by other methods. Only special alloys, such as phosphor-bronze or a manganese-copper alloy made with ferro-manganese contain notable quantities of phosphorus. Phosphorus is also sometimes present in aluminum brass, and a sample was found to contain 0.056 per cent. P to 0.22 Fe. Where phosphorus and arsenic are used as deoxidizers, only a very small quantity is to be found on analysis.

To properly precipitate iron, aluminum, or bismuth by ammonia it is necessary to avoid a large excess of the reagent, but in adding ammonia to re-solution of the copper salt an excess must be added and retained. Using test solutions for examination of the use of ammonia and barium hydrate the following results from sixty odd experiments were obtained:

Element.	NH_4HO.	$NH_4HO + Ba(HO)_2$.	Dilution.
Phosphorus	not precipitated.	not precipitated completely.	100 cc.
Arsenic	"	precipitated.	50 cc.
Nickel	"	not precipitated	"
Cobalt	"	"	"
Zinc	"	"	"
Cadmium	"	"	"
Silver	"	"	"
Bismuth	ppt. incomplete.	ppt. complete.	150 cc.
Manganese	"	"	"
Antimony	"	coloration by H_2S, trace in solution.	"
Tin	ppt. complete.	ppt. complete.	"
Lead	"	"	"
Iron	" (?)	"	"

With arsenic in the ammoniacal solution of fifty cc. dilution the precipitation by $Ba(HO)_2$ is complete, as barium ammonium arseniate (Douglas and Prescott, Qual. Anal.). In dilute solutions or on heating the precipitation becomes incomplete. Digestion with alkali sulphide (S_n) does not transpose this precipitate. Phosphorus is precipitated as barium phosphate. With a copper containing known quantities of the minor constituents the following results by the use of ammonia and barium hydrate were obtained: The original copper taken contained 0.03 per cent. Fe and 0.025 per cent. Pb as impurities. Allowance was made in calculating.

Element.	Present.	Taken 10 grams Cu	Taken 20 grams Cu	Taken 30 grams Cu	Taken 40 grams Cu	Taken 50 grams Cu
Arsenic	0079	0053	0051	0081	0079	0073
Tin	0041	0048	0043	0043	0030	0040
Antimony . . .	0048	0051	0050	0042	. .	0045
Lead	0053	0052	0056	0056	0060	0057
Bismuth . .	0028	0030	0030	0026	0029	0034
Cadmium . . .	0295	0309	0307	0291	. .	0221
Phosphorus . .	0032	0024	0037	0029	0021	. . .
Dilution in cc. . .		300	400	*(800)	800	800

The difficulty arising in the use of thirty, forty, or fifty grams of the pig copper came from the separation of the copper-ammonium salts. The dilution was 800 cc. It also takes the equivalent quantity of potassium cyanide to decolorize the filtrate. If

the solution is allowed to stand but thirty to sixty minutes the copper salt is much diminished in quantity and the precipitate appears to be all down. Ten grams and a dilution of 150 cc. works well. The copper-ammonium salts are readily soluble in water on warming, and if arsenic and phosphorus are in the form of iron or other insoluble salt they are not affected by such treatment. The above results were obtained: By dissolving in nitric acid, adding ammonium hydroxide to re-solution of the copper salt followed by addition of excess of barium hydroxide, such excess being quickly indicated by the formation of the crystalline barium carbonate. Allowed to stand 30 to 120 minutes and filtered. Filtrate decolorized by potassium cyanide and precipitated by hydrogen sulphide.

In the July (1893) number of this JOURNAL Mr. Jesse Jones applies a method for the determination of manganese in bronzes based on Ford's method in steel analysis. In the course of the method as described he removes copper by hydrogen sulphide, filters and obtains the manganese from the filtrate. His paper simply describes the course of analysis without entering into any details as to why it was found necessary to remove the copper. In making some analyses for Mr. F. Lynwood Garrison (*Jour. Frank. Inst.*, June to September, 1891), Hannay's reaction, the oxidation and precipitation of manganese as manganese dioxide in the nitric acid solution by potassium chlorate, was applied at once and without removing copper. It was the suggestion of the late Dr. F. A. Genth to try this method as conducted in the analysis of steel and subsequent examination of the filtrate gave negative results for manganese. I have repeated the experiments to find out whether or not removing copper is a source of error and the results given below were obtained on a manganese brass, dissolved in nitric acid and made up to 100 cc. Aliquot portions were then taken, the manganese precipitated by potassium chlorate and titrated in neutral solution by permanganate. The variation is within reasonable limit and shows, I think, that there is no objection to proceeding with a copper alloy in the manner as with steel and that the removal of copper is not essential to accuracy.

00659 00659 00655 00647 00655 00640

I wish to acknowledge the kindness of Prof. F. A. Genth to whose encouragement was largely due the idea of putting these data into form, and of Mr. F. Lynwood Garrison to whom I am indebted for a number of alloys from his collection.

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INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

SUB-COMMITTEE ON METHODS.

BULLETIN No. 1.

ORGANIZATION AND WORK OF THE COMMITTEE.

AT the World's Congress of Chemists, in Chicago, last August, following the papers of Professor J. W. Langley, "On the Work of the Committee on International Standards for the Analysis of Iron and Steel," and of Dr. C. B. Dudley, "On the Need of Standard Methods for the Analysis of Iron and Steel, with Some Proposed Standard Methods," was a brief discussion, which resulted in the reference by that body of the whole subject of standard methods for the analysis of iron and steel, to the Committee on International Standards for the Analysis of Iron and Steel. That committee, it will be remembered, consists of seven chemists, in each of five different countries; namely, England, France, Germany, Sweden, and the United States. The American Committee was appointed jointly by the American Society of Civil Engineers, and the University of Michigan, with Professor J. W. Langley, Case School of Science, Cleveland, Ohio, as chairman. The other members of that Committee were W. P. Barba, Midvale Steel Works, Nicetown, Philadelphia, Pa., A. A. Blair, 406 Locust street, Philadelphia, Pa., Professor Regis Chauvenet, President State School of Mines, Golden, Colorado, Professor T. M. Drown, Mass. Inst. Technology, Boston, Mass., Dr. C. B. Dudley, Chemist Penn'a. R. R. Co., Altoona, Pa., and Porter W. Shimer, Easton, Pa.

Following the reference of the subject to this committee, it

was decided after consultation to appoint a sub-committee, to take up the question of standard methods. The sub-committee is constituted as follows: W. P. Barba, A. A. Blair, T. M. Drown, Porter W. Shimer and C. B. Dudley, Chairman.

The sub-committee held an organizing meeting at the office of A. A. Blair, 406 Locust street, Philadelphia, on December 13, all the members being present. The object of the meeting was to map out the work. It was agreed as follows:

First. That Mr. Blair should submit a form of circular to go to the iron and steel chemists of the country, asking for a brief outline of the methods which they prefer, and the reasons for all the important points of their methods.

Second. That the work of the committee should comprehend the recommendation of standard methods to be used as the basis of commercial transactions, and when any of these methods could not be used in steel works in daily practice, on account of time required, an alternative rapid method should be recommended, and its limitations defined.

Third. That the members of the committee should draw up each proposed standard method in writing, with some minuteness, and give the reason for each important point, these written drafts to be sent to the chairman, to be duplicated, and sent to every member of the committee. Later, the points agreed upon are to be edited by some one member of the committee.

Fourth. That only one element should be embraced in a method.

Fifth. That the first method to be taken up, should be phosphorus in steel.

Sixth. Mr. Barba offered to furnish to each member of the committee, a suitable quantity, not less than a pound or so, of borings of three (3) different kinds of steel; namely, one of from 0.01 to 0.02 phosphorus, carbon about 0.90, and silicon about 0.40; another with phosphorus not far from 0.06, carbon 0.50 to 0.60, silicon 0.25 to 0.30, and arsenic 0.15 per cent. The above two, to be crucible steel. Another sample of open hearth steel of carbon 0.90 to 1.05, phosphorus 0.02 to 0.04, manganese 0.30 to 0.40, silicon 0.20 to 0.25, sulphur 0.02 to 0.04 and copper anywhere below 0.10.

Seventh. Dr. Dudley offered to furnish to each member of the committee, a like amount of borings from a sample of Bessemer steel of from, 0.10 to 0.12 phosphorus, carbon about 0.50, manganese 0.80 to 1.00, silicon 0.02 to 0.05, sulphur 0.07 to 0.10 and copper from 0.07 to 0.10. These samples of steel to be used in deciding various questions that may come up in regard to proposed methods.

A very earnest feeling was manifested at the meeting of the sub-committee, and the outlook for some good work, is apparently very favorable.

APPROVED:

J. W. LANGLEY,
Chairman Com. on Int. Standard.

CHAS B. DUDLEY,
Chairman Sub-Committee.

NEW BOOKS.

A MANUAL OF PRACTICAL ASSAYING. BY H. van F. FURMAN.

The constantly increasing demands made on metallurgical chemists for rapid work makes the appearance of Mr. Furman's book very timely; for while there are numerous text-books on assaying, and complete treatises for the iron-works chemist, no work until this has so completely embodied the methods now in use by the chemists of the silver, lead, and copper smelters of the west, and it is for these especially that the book is written.

On this account it would seem more appropriate to have included technical analysis in the title, for while the term assaying may doubtless be properly used as meaning more than fire assaying, it can hardly be construed into covering the contents of this book, which contains methods not in common use, by the technical chemist at least, and which in actual practice would probably be looked up in more detailed and specialized works. It would, however, hardly be just to criticise the author for making his manual as complete as possible, providing good judgment is used in selecting the methods, which is the case in all but a very few instances.

Part I, which is introductory, and includes chapters giving useful details as to reagents, apparatus, blowpipe reactions, etc.,

contains a chapter on sampling worthy of special mention. This chapter gives a thorough description of both hand and mechanical sampling as applied to the crude material, and to the finished products of the smelter. When it is remembered that the value of all the subsequent work depends upon having a good sample to start with, it can easily be seen that a knowledge of this subject is of great importance. As those accustomed to smelter work know, inaccurate sampling, either real or supposed, is the source of constant disputes; and anyone not already familiar with the various methods can read this chapter with profit.

Part II describes the methods for the separate determination of all the elements which need be considered in a technical manual; including a very full description of the fire assay for gold, silver, and lead.

Of course in a limited space no review can be attempted of all the methods given in this part of the book; but in general it can be said, that while there are perhaps occasional details which could be advantageously modified, they are methods which have stood the test of actual use under the trying conditions of smelter laboratories, where rapidity is the first and accuracy the second essential.

Some of the methods given here, while in constant use in the west, have not received the attention they deserve at the hands of analytical chemists in general; most conspicuous of these are the methods of A. H. Low for zinc, of H. H. Alexander for lead, and of F. C. Knight for lead, when used with the skill coming from practice, and with a proper understanding of the conditions involved, these methods, while essentially rapid, give results of a high degree of accuracy; they have a place indeed in the first rank of volumetric determinations.

The student of technical analysis can safely accept the methods given in Part II as carefully selected and reliable, and rendered additionally valuable by the liberal use of foot notes in referring to the original sources of information.

Part III is devoted to the description of special assays and analyses. The most important chapters here, of course, are those dealing with subjects which come up with more or less con-

stancy in smelter laboratories and assay offices; such as the assaying of the different kinds of bullion and mattes, and the analysis of slags, and these the author has treated very satisfactorily. In addition, among somewhat miscellaneous matter, are chapters on the analysis of gases, water, phosphates, etc., which in the absence of the standard text-books on these subjects will furnish a guide for doing such work, although the practice of trying to do chemical work without the proper fundamental knowledge cannot be too strongly deprecated.

Part IV, the last, includes chapters on the writing of chemical equations and stoichiometry, which are good in themselves, but of doubtful usefulness in a book of this kind, unless, perhaps, they are considered chiefly as preparing the way for the final chapter on the calculation of lead blast-furnace charges; a subject of much importance, and one which the author, from his own experience, is well fitted to treat.

A copious and well selected set of tables concludes the volume.

In his expressed object to "fill * * the wants of technical chemists" the author has certainly succeeded quite well, perhaps even too well; for with a volume of condensed information at hand the race of "machine" chemists, with which the west is already overstocked, will probably be increased. For this evil some of the western technical schools are primarily to blame. So long as they see fit to give a student a certificate of competency as a chemist or assayer when his stock of knowledge consists of an assortment—well selected it is true—of rule-of-thumb methods, just so long will the demand for this kind of education exist; and Mr. Furman, I fear, has unintentionally made it easier to get. While his book will be most useful to the well-trained analyst who can use the methods with discrimination, it can also be made to answer the purpose of the mechanical chemist as well.

L. G. EAKINS.